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Aspects Of Sulfene Chemistry

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by

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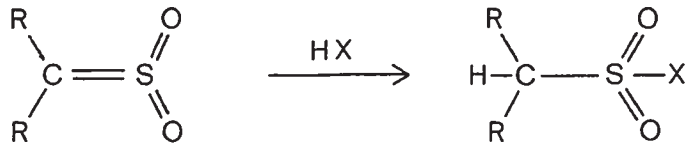
For the best and safest method of philosophizing seems to be, first diligently to investigate the properties of things and establish them by experiment, and then to seek hypotheses to explain them. For hypotheses ought to be fitted merely to explain the properties of things and not attempt to predetermine them except in so far as they can be an aid to experiments.

ISAAC NEWTON

ABSTRACT

Sulfenes are believed to be intermediates in the base-induced transformation of alkanesulfonyl chlorides to derivatives such as acids, sulfonate esters, and sulfonamides. Although good evidence for their existence has been obtained, little was known about the nature of these intermediates. In this thesis a number of investigations are reported which increase our knowledge in this area.

It is generally accepted that sulfenes react like Lewis acids towards basic reagents such as water, alcohols, amines, etc. (called sulfene "traps"). The rates of these reactions



are unknown but are extremely fast. A number of competition experiments were done, in which sulfenes were generated in the presence of equimolar quantities of pairs of traps. The relative rates of reaction of the traps with the sulfene were obtained by determining product ratios. These experiments provided new information about sulfenes. The more important findings were: sulfenes in general react fastest

with the strongest bases (*i.e.* secondary amine > aromatic amines > alcohols); and "hard" bases (in the Pearson sense) react faster than "soft" bases, indicating that sulfenes themselves are hard acids.

Usually when sulfenes are generated in the presence of deuterated traps (*e.g.* CH_3OD), the products are mono-deuterated. It was found that when unhindered bases (*e.g.* quinuclidine) were used to generate sulfenes, perdeuterated products were obtained. A mechanism was proposed to explain this phenomenon.

The last part of this thesis concerns the mechanism of sulfene formation, and constitutes an extension of earlier work on this topic. The rate of sulfene formation was found to depend linearly upon the basic strength of the amine, and no dependence on stereochemistry could be detected. This corroborates earlier evidence that the mechanism involves an abstraction of hydrogen in the rate-determining step. Evidence regarding the deuterium isotope effect and the effect of traps on the rate of reaction was also considered.

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PART I

GENERAL INTRODUCTION

Although sulfenes have been mentioned as possible reaction intermediates since 1908, convincing evidence for their existence has been gathered only in the last ten years. Inasmuch as the literature of sulfenes has become quite diverse and extensive, no attempt will be made here to give a general review of the subject, and the interested reader is referred to the review by Opitz (1). However, the subject matter of each of the parts of the thesis will be preceded by an introduction treating the relevant background material.

Sulfenes may be formulated as $RR'C = SO_2$, and may be regarded as sulfur analogues of ketenes, or as a sulfur trioxide derivative with an alkylidene group in place of one of the oxygens. They are highly reactive intermediates in a wide variety of reactions. One of the most convenient means of generating sulfenes is by the action of base, such as triethylamine, pyridine, or sodium hydroxide, on a sulfonyl chloride having an α-hydrogen (2,3). When water, alcohols, or amines (sulfene "traps") are included in the reaction mixture, the products are sulfonic acids, esters, and amides, respectively.

With deuterated traps (*e.g.* deuterium oxide, methanol-*d*), monodeuterated products are obtained (2, 3). Thus sulfenes appear to react as Lewis acids, reacting at the sulfur atom with nucleophilic traps. In the absence of traps, the products of the reaction of phenylmethanesulfonyl chloride and triethylamine are *trans*-stilbene, *cis*-stilbene episulfone, or the *cis* and *trans* thiobenzoyl chloride *S*-oxides, depending on experimental conditions (4). The appearance of these products was explained in terms of phenylsulfene as intermediate. The sulfenes generated by base-induced dehydrohalogenation have never been directly observed, but the deuteration experiment mentioned above constitutes strong evidence for their existence. In addition, kinetic evidence for the generation of sulfenes has been obtained (5).

When sulfenes are generated in the presence of enamines, four-membered ring adducts of the sulfene are obtained (1). This is considered excellent evidence for the intermediacy of sulfenes, since the products obtained cannot be accounted for by assuming a non-sulfene step-wise addition of the sulfonyl chloride to the enamine (6).

A particularly interesting example of the generation of sulfenes by base-induced dehydrohalogenation of sulfonyl chlorides was discovered by Opitz and Bücher (7). When methanesulfonyl chloride was treated with trimethylamine at -20°, a "sulfene adduct", formulated as $CH_3SO_2\overset{-}{C}HSO_2\overset{+}{N}(CH_3)_3$, was obtained in good yield. This result further demonstrates

the Lewis acid nature of the sulfene sulfur atom, by its ability to coordinate with the amine nitrogen.

An alternative means of generating sulfenes in solution is by the reaction of diazoalkanes with sulfur dioxide. In the presence of water (8), alcohols (8), and amines (9), typical sulfene products (sulfonic acids, esters, and amides) are formed. In the absence of traps, diphenyldiazomethane and sulfur dioxide give benzophenone or tetraphenylethylene episulfone, depending on conditions (8). These products were rationalized by postulating diphenylsulfene as an intermediate.

Evidence has been gathered for the intermediacy of sulfenes in a number of quite different reactions. These include the photolysis of unsaturated cyclic sultones (10) and sultams (11), the thermolysis of thiete 1,1-dioxide and 3-thietanol 1,1-dioxide under various conditions (12), the low pressure thermolysis of chlorosulfonylacetic acid (13), and the loss of chloride ion from the α-chloroethylsulfinate anion in the presence of sulfene traps such as water, *p*-toluidine, and an enamine (14).

In the sections that follow, both the mechanism of formation of sulfenes, and their behavior in the presence of traps and bases, is investigated. In Part II, information is presented about the relative rates of reaction of sulfenes with various traps. Part III describes the reaction of

sulfonyl chlorides with unhindered bases such as quinuclidine and trimethylamine, in the presence of deuterium oxide and other deuterated traps. The products were found to be perexchanged rather than monodeuterated, and an explanation for this effect is proposed. Finally, further evidence for the mechanism of sulfene formation by the action of amines on sulfonyl chlorides is presented in Part IV.

PART II

COMPETITION EXPERIMENTS

A. Introduction

Although we now have a fairly detailed picture of the mechanism of sulfene formation (see Part IV and ref. 5), very little is known at present regarding the relative reactivity of sulfenes towards different reagents (sulfene "traps"). It is known that sulfenes apparently react very fast. Phenylsulfene has never been directly observed in the reaction of phenylmethanesulfonyl chloride and triethylamine, even in the absence of added traps. The second-order rate constant for this reaction (at -25°) has been estimated as 38 l. $mole^{-1}$ sec^{-1} (15), so the reaction of sulfenes to form products like stilbene must be much faster. In the presence of a trap, such as alcohol, close to quantitative yields of sulfonate esters rather than stilbene are formed, and this rate of trapping must be still faster.

There are several good reasons why it would be informative to know the relative rates of reaction of sulfenes with various traps. For instance, it would be useful if sulfenes

could be identified by their characteristic reactivity. This would be especially helpful when traditional methods of indicating sulfene intermediacy fail (e.g. in Part III, products were perexchanged rather than monoexchanged, although it was felt likely that sulfenes were nevertheless involved). Knowledge of relative trapping rates should prove useful in synthetic problems. Also, the information is of theoretical interest. Very little is known at present about bonding, polarity, electrophilicity, or geometry of sulfenes, and some progress in this direction may be made by investigating sulfene reactivity.

Because the rate of trapping is so high, it is impossible to measure the rate constants directly. However, the reactions lend themselves well to studying relative rates by product analysis. Sulfene products such as sulfonate esters and sulfonamides are stable under reaction conditions, can be isolated in high yield, and are readily identified by n.m.r. and i.r. spectroscopy. The reactions are irreversible, and side reactions are usually minimal. Therefore the ratio of products obtained should be equal to the ratio of the rate constants leading to their formation (16). Some cases are exceptions to the above statements (see sections B and C), and the sulfene product initially formed reacts further. When these situations were encountered, special methods were devised to compute the ratio of rate constants.

A series of exploratory experiments was carried out, usually using phenylmethanesulfonyl chloride as a source of phenylsulfene. Equimolar amounts of trapping agents were added, followed by the tertiary base. In sections B and C, pairs of "hard" and "soft" (in the Pearson sense (17)) bases were used as traps, to determine if sulfenes behave like hard or soft acids. In section D, a series of anilines were used in pairs as traps, to investigate the relationship of basicity of the trap to the rate of reaction with sulfene. A variety of other competition reactions were done in section E, to gain a broader view of trap reactivities.

B. Competition Reaction with Fluoride and Chloride Ions

It was suggested in the general introduction that sulfenes bear a formal relationship to sulfur trioxide. The comparison appears to be justified, since sulfenes, like sulfur trioxide, seem to react like Lewis acids. Further insight into this relationship may be gained by comparing the "hardness" of sulfenes and sulfur trioxide. The latter has been designated a hard acid by Pearson (17), on the basis of its tendency to form compounds of greater stability with hard bases than soft. In order to classify sulfenes as either hard or soft acids, a competition reaction was done with fluoride ion and chloride ion. Fluoride ion is generally regarded as very hard, whereas chloride is often considered intermediate.

A direct comparison of fluoride and chloride revealed fluoride to be much harder than chloride (18).

The product of the reaction of a sulfene with fluoride ion is a sulfonyl fluoride. These compounds are stable and may be isolated in high yield. The product of attack by chloride ion is of course a sulfonyl chloride, and under the usual conditions is identical with starting material. But if a deuterated sulfonyl chloride, such as phenylmethane-d_2-sulfonyl chloride is used under conditions where exchange is possible, the product will be largely monodeuterated. This sulfonyl chloride will react further, losing either D or H, to produce fully protiated phenylsulfene and phenylsulfene-*d*. If fluoride as well as chloride is present, ultimately all the product will be sulfonyl fluoride. Any perexchanged sulfonyl fluoride must have its origin in attack by chloride, and the extent of chloride attack may be estimated by calculations.

The experiment was carried out by preparing a solution of triethylamine, and equimolar quantities of triethylammonium fluoride and triethylammonium chloride in methylene chloride, and adding it with swirling to a solution of phenylmethane-d_2-sulfonyl chloride in methylene chloride. Quantities were chosen so that there would be a large excess of active protium in solution during the entire reaction (minimum of 97% H), so that any re-addition of deuterium may

be ignored, to a first approximation. The reaction was complete in less than ten seconds. The product, phenylmethanesulfonyl fluoride, was isolated in good yield. The isotopic composition of the product was determined by mass spectrometry and by combustion analysis (J. Nemeth). The results obtained either way agreed very closely. In addition, the results were confirmed by n.m.r. spectroscopy. The values may be found in Table I.

In addition to the experiment described above, a control experiment was done without triethylammonium chloride, but with the same quantities of the other components. These results are also tabulated in Table I.

A significant amount of unexchanged sulfonyl fluoride was found in both experiments. This material likely resulted from a direct displacement reaction by fluoride ion on the sulfonyl sulfur. In order to learn more about this reaction, an experiment was done as above, but using pyridine instead of triethylamine, and pyridinium fluoride (no chloride). Since pyridine is a much weaker base than triethylamine, the rate of sulfene formation will be much slower (5, 15). If a displacement by fluoride occurs, it should be the predominant reaction in the pyridine experiment. The sulfonyl fluoride product was found to contain about 80% deuterium at the α-carbon, thus supporting the displacement mechanism.

Further evidence was found in the reaction of phenylmethanesulfonyl chloride with tetraethylammonium fluoride in

TABLE I

Deuterium analyses for phenylmethanesulfonyl fluoride, obtained from the fluoride and chloride ion competition experiment and the fluoride ion control experiment.

	Mass Spectroscopy Results (mole %)	
	F^- and Cl^-	F^-
CH_2	8.8	3.9
CHD	81	78
CD_2	9.7	18
D atoms[a]	1.01	1.14

	Combustion Results (mole %)	
	F^- and Cl^-	F^-
excess D, atom %	14.70	16.55
D atoms[b]	1.03	1.16

a. D atoms at α-carbon, calculated from the mass spectroscopy results.

b. D atoms at α-carbon, calculated from the combustion results.

chloroform. The reaction was over in about one minute, and produced the fluoride in excellent yield. The evidence therefore strongly suggests that the unexchanged sulfonyl fluoride arises from a non-sulfene reaction, and should be ignored in the treatment that follows.

Of primary interest is the fully exchanged sulfonyl fluoride. The small amount (3.9 mole %) that appeared in the control experiment may be entirely accounted for by the protium in the sulfonyl chloride starting material. The amount of this protium was about 6.2 atom percent, based on the Nemeth analysis (26.80 atom % D means 93.8 atom % D at the α-carbon). This is equivalent to 12.4 mole % $C_6H_5CHDSO_2Cl$ and a negligible amount of $C_6H_5CH_2SO_2Cl$. Assuming a deuterium isotope effect of 2.6 (19,5), the initially formed sulfene will contain about 3.4 atom % protium. All of this protium will turn up in the product as perexchanged material ($PhCH_2SO_2F$), and it is close to the observed value of 3.9 mole %. Therefore a correction should be applied to both reactions, by subtracting 3.9 from the amount of diexchanged sulfonyl fluoride.

The result of making the corrections mentioned above, and normalizing the results so that the values add up to 100%, gives the values in Table II.

TABLE II

Deuterium content for sulfonyl fluorides, corrected for non-sulfene reaction and protium in starting material. (Values in mole %.)

	F^- and Cl^-	F^-
CH_2	5.7	0
CHD	94	100
Ratio $\left(\frac{CHD}{CH_2}\right)$	16.5	-

The competition experiment contained a significant amount of perexchanged product ($PhCH_2SO_2F$). The appearance of this material (after the corrections in Table II) is due solely to the introduction of triethylammonium chloride. Since the cation was also present in the control experiment, and led to no noticeable perexchange, it is unlikely that it could influence the outcome in any significant way in the competition experiment. This leaves chloride as the only factor which could have caused this perexchange. The most likely mechanism is the attack of phenylsulfene by chloride ion already mentioned. Qualitatively the conclusion is that a definite amount of attack by chloride ion occurs.

The possibility of attack by chloride on a sulfene has been proposed by Durst to explain perexchange (20). When

phenylmethane-d_2-sulfonyl chloride was treated with triethylamine in methylene chloride in the presence of triethylammonium chloride, stilbene was produced. The olefinic position contained only 0.80 D. When triethylammonium phenylmethanesulfonate was used instead of the chloride, the deuterium content was 1.50 D. The result was rationalized by postulating readdition of the elements of HCl to the sulfene. (Presumably the sulfonate ion does not possess the required reactivity for readdition.)

It is possible to calculate the relative rates of attack of fluoride and chloride ion in a semiquantitative way by considering the following reaction scheme:

$$\mathrm{PhCD_2SO_2Cl} \longrightarrow \underset{\underline{\underline{A}}}{\mathrm{PhCD{=}SO_2}} \xrightarrow[F^-]{k_1} \underset{\underline{\underline{B}}}{\mathrm{PhCHDSO_2F}}$$

$$k_3 \Big\downarrow\Big\uparrow k_2 \; \mathrm{Cl^-}$$

$$\underset{\underline{\underline{C}}}{\mathrm{PhCHDSO_2Cl}} \xrightarrow{k_4} \underset{\underline{\underline{D}}}{\mathrm{PhCH{=}SO_2}}$$

Phenylsulfene-d ($\underline{\underline{A}}$) may be attacked by either fluoride or chloride ion. The ratio of the rate of attack by fluoride to the rate of attack by chloride may be designated by $x = k_1/k_2$. Sulfonyl chloride $\underline{\underline{C}}$ will eliminate HCl or DCl (giving $\underline{\underline{A}}$ or $\underline{\underline{D}}$), and the deuterium isotope effect h is k_3/k_4. The paths leading to $\underline{\underline{B}}$ and $\underline{\underline{D}}$ may be regarded as irreversible; in

the case of D, this is because the proton pool is assumed to contain no deuterium. All of D ultimately becomes perexchanged sulfonyl fluoride. Hence the ratio of the rates of formation of B to D is equivalent to the ratio of $PhCHDSO_2F$ to $PhCH_2SO_2F$ in the product. This ratio may be calculated in terms of x and h.

The initially formed sulfene A reacts very fast, and forms B and C in the ratio of k_1 to k_2. For every mole of C that forms, x moles of B form. C is unstable, and decomposes to form $k_4/(k_3 + k_4)$ of D and $k_3/(k_3 + k_4)$ of A. At this point we have x moles of B and $k_4/(k_3 + k_4)$ of D, plus a quantity of A. The ratio of B to D is

$$\frac{B}{D} = \frac{x(k_3 + k_4)}{k_4} = x\left(\frac{k_3}{k_4} + 1\right)$$

$$= x(h + 1).$$

The remaining A will react to form B and D in the same ratio as given above. The trapping rate ratio is

$$x = \frac{B/D}{h + 1}.$$

The value of B/D is 16.5 (see Table II). The deuterium isotope effect h has been estimated to be 2.6 for the reaction of phenylmethane-*d*-sulfonyl chloride and triethylamine in dioxane (19, 5). Substituting the values of B/D and h into

the above equation gives x = 16.5/3.6 = 4.6. The trapping rate ratio is therefore 4.6 : 1 for fluoride to chloride ion.

The error in estimating B/D is probably less than ± 10%, but the error in the value for h is unknown. The value of 2.6 may not be accurate for these experimental conditions. If a value of ± 10% is arbitrarily assumed, the trapping rate ratio is found to have an error of ± 7% (this may be seen by substituting appropriate values into the equation).

The results clearly indicate a preference of phenylsulfene for fluoride ion, the hard base, rather than chloride ion. This evidence suggests that phenylsulfene, like sulfur trioxide, is a hard acid.

It is noteworthy that the rate ratio of 4.6 is as low as it is. Most other competition experiments gave similar moderate values (see later in this chapter). Such lack of discrimination in competition experiments is characteristic of reactions having a low transition state energy. This may be demonstrated theoretically by considering the Arrhenius equation, $k = Ae^{-E/RT}$. For two competing reactions which proceed at rates k_1 and k_2, the rate ratio is

$$\frac{k_1}{k_2} = \frac{A_1 e^{-E_1/RT}}{A_2 e^{-E_2/RT}}$$

$$= \frac{A_1}{A_2} e^{(E_2-E_1)/RT}$$

If the factor A_1/A_2 is assumed to be $\sim$1 for simplicity, it is seen that the rate ratio depends upon the difference in activation energies. For very fast reactions (the kind expected for sulfene trapping reactions), both E_1 and E_2 will be small, and the difference will be even smaller. In the present experiment, the rate ratio of 4.6 corresponds to a difference in activation energies of $\sim$0.9 Kcal.

Although the rate ratio obtained in this experiment is reproducible under the reaction conditions chosen, there is good reason to believe that to some extent the apparent trapping rate ratio depends on the concentration of the base (see section D and E, especially the diethylamine experiments). Ratios generally seem to rise as the base becomes more dilute. Therefore the value of 4.6 is felt to be an apparent value, accurate only under the reaction conditions of the present experiment. However, it will serve under the circumstances, indicating semiquantitatively that fluoride ion reacts decisively faster than chloride.

C. Competition Reaction with Mercaptan and Alcohol

Further evidence was sought to confirm the hard acid nature of sulfenes. An experiment with an alcohol and a mercaptan as sulfene traps was therefore carried out. Alcohols are hard bases, and mercaptans are typical soft bases (17). If the fluoride-chloride experiment correctly indicated

that sulfenes are hard acids, the alcohol would be expected to react faster than mercaptan.

The reaction of sulfenes with alcohols produces sulfonate esters, which are fairly stable compounds. In particular, it was shown that isopropyl phenylmethanesulfonate, from the reaction of phenylmethanesulfonyl chloride with pyridine and isopropyl alcohol, was stable under the reaction conditions of the competition experiment. It could be isolated in high yield (93%).

On the other hand, the product of the reaction of phenylsulfene with benzyl mercaptan produces benzyl phenylmethanethiolsulfonate, which is unstable under the reaction conditions. The thiolester reacts with excess mercaptan to give phenylmethanesulfinic acid and dibenzyl disulfide. The extent of reaction with mercaptan may nevertheless be determined by measuring the amount of sulfinic acid produced. This is most conveniently done by chlorinating it and converting it to the sulfonyl chloride.

The experiment was carried out by dissolving pyridine and equimolar quantities of isopropyl alcohol and benzyl mercaptan in methylene chloride. This solution was added to a solution of phenylmethanesulfonyl chloride, with swirling. The reaction was complete in 30 min. Pyridine was chosen as the tertiary base since it is much weaker than triethylamine, and less likely to cause extensive dissociation of the mercaptan. It is known to give phenylsulfene with phenylmethane-

sulfonyl chloride (2).

The yield of ester from the competition experiment was found to be 84 mole %. After treating the sulfinic acid with chlorine gas, sulfonyl chloride was isolated in 7.3% yield. On the basis of these figures, the alcohol appears to react faster than the mercaptan by a factor of 11.5.

Several experiments were done to ensure that the interpretation of the results above was in fact correct. The competition experiment was repeated, but instead of the sulfonyl chloride, an equimolar amount of the thiolester was used. The sulfinic acid was isolated as the sulfonyl chloride in 100% yield. The possibility that the thiolester might eliminate mercaptan under reaction conditions to form a sulfene was excluded by this experiment, since no isopropyl phenylmethanesulfonate was produced.

It was also shown that the sulfinic acid was in fact a sulfene product. In a reaction of phenylmethane-d_2-sulfonyl chloride with pyridine and excess mercaptan, the sulfonyl chloride isolated was found to be phenylmethane-d-sulfonyl chloride.

When the competition experiment was repeated without isopropyl alcohol, the sulfinic acid was obtained (as sulfonyl chloride) in only 44% yield. It is not known why the yield is low, when the thiolester itself gives a 100% yield (as sulfonyl chloride). In view of this low yield, the 7.3 %

yield in the competition experiment may be low by approximately a factor of two. The trapping rate ratio may therefore be expressed as 6 - 11.5 : 1, in favor of the alcohol. As in the fluoride and chloride experiment, the ratio is moderate.

The alcohol and mercaptan experiment confirms the conclusion of the fluoride and chloride experiment, by demonstrating that phenylsulfene reacts faster with hard bases than with soft. This is further evidence that sulfenes react like hard acids.

D. Competition Reactions with Aniline Derivatives

In order to find out more about the reactivity of sulfenes, a series of experiments was done in which various substituted anilines were used as traps. Since sulfenes appear to react as Lewis acids, we might expect strongly basic traps to react faster with them than weakly basic traps. The basic strength of aromatic amines may be varied through a considerable range by changing the substitution on the ring. (The pK_a's of *p*-anisidine and *m*-nitroaniline are 5.29 (21) and 2.47 (22), a difference of 700 fold.) It is reasonable to expect a stronger base like *p*-anisidine to react faster with sulfene than *m*-nitroaniline.

The products obtained in these experiments are sulfonamides, which are very stable compounds. In every case the

sulfonamides were prepared separately under conditions similar to the competition experiments. The yields were high. One of the traps was usually *p*-toluidine, because the sulfonamide obtained has a convenient methyl group, which facilitates analysis in the n.m.r.

The experiments were conducted by preparing a solution containing triethylamine and equimolar quantities (usually 20 mmole) of the traps in methylene chloride. This solution was added with swirling to a solution of phenylmethanesulfonyl chloride (usually 2 mmole). The product mixture was isolated by extraction, and the composition determined by n.m.r. spectroscopy and confirmed by i.r. spectroscopy. The trapping rate ratio was computed by dividing the yields of the products.

In experiments where *p*-toluidine was used as one of the traps, rate ratios were calculated relative to a value of 1.00 for toluidine. The results of these experiments may be found in Table III. A number of experiments were done with aniline as the reference trap, in order to demonstrate that the outcome is independent of the choice of reference trap. In these experiments, the values were calculated relative to a value of 1.00 for aniline, and may be found in Table IV.

The logarithms of the trapping rate ratios were calculated for the experiments using *p*-toluidine as one of the traps, and a Hammett plot was drawn by plotting the values

TABLE III

Competition reactions of *p*-toluidine and other aromatic amines for phenylsulfene, generated by the reaction of triethylamine on phenylmethanesulfonyl chloride in methylene chloride.

Aniline Substituent	Product[a]		Rate Ratio[b]	Estimated Error (%)	Log Ratio
	p-toluidide	Subst. Amide			
p-OCH_3	46	54	1.17	3	.07
p-CH_3	-	-	1.00	3	.00
H	62	38	0.61	3	-.21
m-OCH_3	66	34	0.51	3	-.29
p-Cl	73	27	0.37	10	-.43
m-Cl	81	19	0.24	15	-.62
m-NO_2	89	11	0.12	20	-.92

a. Product of the competition reaction in mole %.

b. Rate of trapping of the substituted aniline relative to the rate of trapping of *p*-toluidine.

TABLE IV

Same as Table III, except that the experiments were done with aniline as reference trap.

Aniline Substituent	Product[b]		Rate Ratio[c]	Est'd Error (±%)	Log Rate Ratio
	Anilide	Subst. Amine			
p-CH_3[a]	38	62	1.63	3	.21
H	-	-	1.00	3	.00
m-OCH_3	55	45	0.82	3	-.09

a. See also previous table.

b. Product of the competition reaction in mole %.

c. Rate of trapping of the substituted aniline relative to the rate of trapping of aniline.

against the σ values of the substituents (the σ values used were those compiled by McDaniel and Brown (23)). The plot for the aniline experiments is drawn on the same graph for comparison. See Fig. I.

A good straight line was obtained for the *p*-toluidine plot, with a slope (ρ) of -1.04. The aniline plot has only three points, but the slope of -1.05 is essentially identical to the *p*-toluidine slope. The moderate and negative value of ρ indicates that a partial positive charge develops on the nitrogen atom in the transition state. This scheme is con-

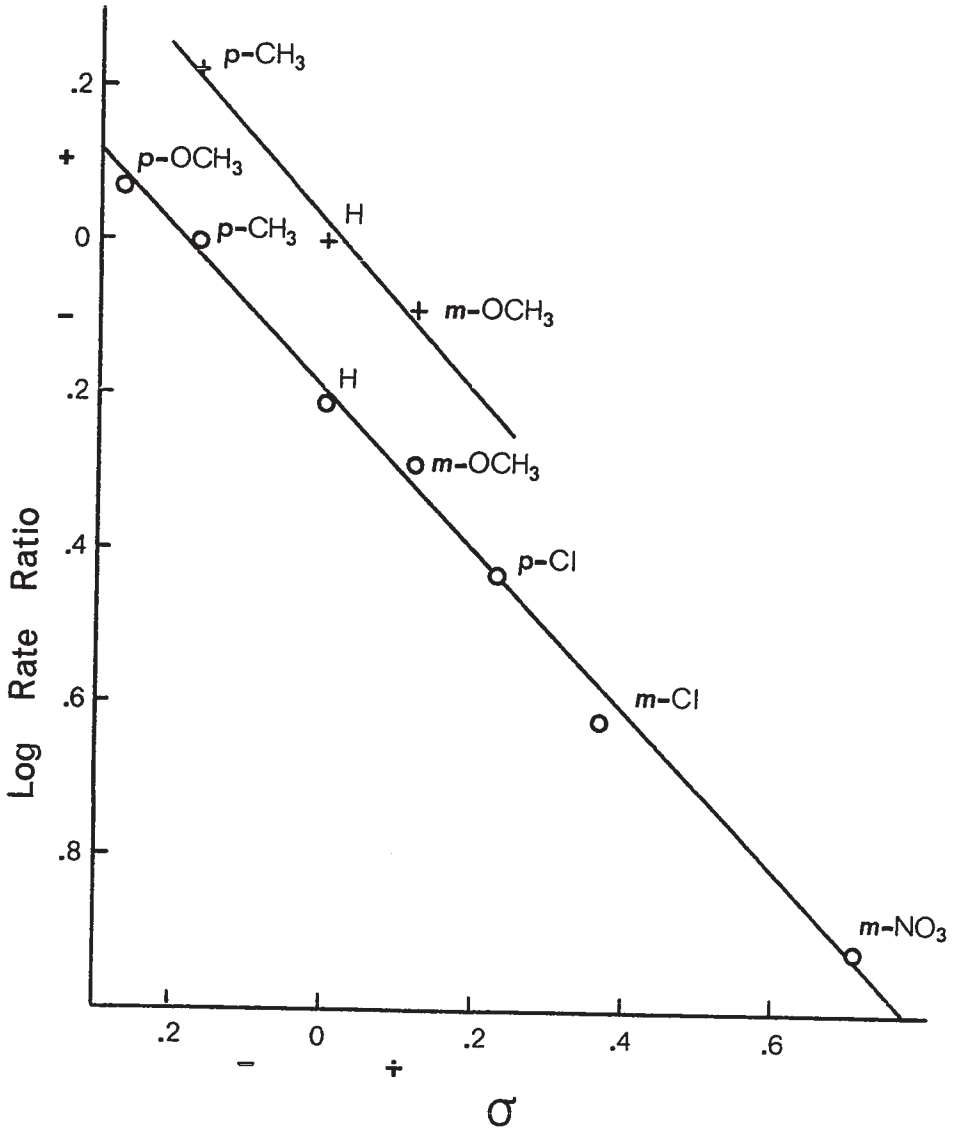


Fig. I. Hammett plot, showing log of the relative trapping rates of aniline derivatives against σ values. +Experiments using aniline as one of the traps o using *p*-toluidide as one of the traps.

sistent with the sulfene reacting as a Lewis acid with a basic trap. The regular increase in trapping rate with increasing basicity of the amine also demonstrates that while sulfenes are reactive entities, the rate of trapping is not diffusion controlled.

A complication was encountered in a number of competition experiments, in which the sulfonamides were fairly acidic (*i.e.* with the *m*-chloroanilide, *p*-chloroanilide, and *m*-nitroanilide). When the traps were *p*-toluidine and *m*-chloroaniline, 2.5% of the reaction product was found to be bis(phenylmethanesulfon)-*m*-chloroanilide. The source of this material must have been the ionized form of phenylmethanesulfon-*m*-chloroanilide, one of the reaction products, which served as a sulfene trap. The sulfonanilide anion apparently is quite an efficient trap. Its concentration was much lower than the other traps, yet a surprisingly large amount of it succeeded in trapping the sulfene.

In order to reduce the amount of bis compound, the amount of triethylamine was reduced in the experiments with *m*-chloroaniline and *m*-nitroaniline (but it was still in excess). The experiment with *p*-toluidine and *p*-anisidine was done with both the usual amount of triethylamine and the reduced amount. The rate ratios were fairly close (1.17 and 1.27, respectively). The increase of 10% in the rate ratio may be significant rather than merely experimental error. In section E, the rate ratio

for a competition reaction with diethylamine and *p*-toluidine increased sharply when the triethylamine was left out entirely.

The bis compounds represent side reactions, and need to be corrected for. Since each mole of bis compound was derived from the corresponding sulfonamide, the trapping rate ratios in Tables III and IV were calculated by including the bis compound mole for mole with the corresponding sulfonamides.

E. Other Competition Reactions

This section describes a number of miscellaneous trapping experiments which serve to outline further the reactivity of sulfenes towards various amine and alcohol traps. Although the experiments are of an exploratory nature, some interesting conclusions may be derived from them.

1. Experiments with Various Amines

In addition to the series of experiments with aromatic amines described in section D, a number of other competition experiments with amines were done. They may be found in Table V.

The experiment with methanesulfonyl chloride using *p*-toluidine and aniline was similar to the corresponding experiment with phenylmethanesulfonyl chloride described in

TABLE V

Competition reactions of various amines for sulfene and phenylsulfene, generated from the corresponding sulfonyl chlorides. Methylene chloride solvent.

Sulfonyl Chloride	Base	Trapping Agents A	Trapping Agents B	Yields (%) A	Yields (%) B	Rate Ratio
CH_3SO_2Cl	Et_3N	*p*-toluidine	aniline	65	32	.49
$PhCH_2SO_2Cl$	pyridine	*p*-toluidine	aniline	68.5	27.5	.41
$PhCH_2SO_2Cl$	Et_3N	*p*-toluidine	Et_2NH	24	70.5	3.0
$PhCH_2SO_2Cl$	(Et_2NH)	*p*-toluidine	Et_2NH	6.2	91	15

TABLE VI

Competition reactions with phenol and isopropyl alcohol.

Sulfonyl Chloride	Base	Trapping Agents A	Trapping Agents B	Yields (%) A	Yields (%) B	Rate Ratio
CH_3SO_2Cl	Et_3N	*p*-toluidine	PhOH	15	82	5.5
$PhCH_2SO_2Cl$	Et_3N	*p*-toluidine	PhOH	17	78	4.5
$PhCH_2SO_2Cl$	pyridine	*p*-toluidine	PhOH	62	35	0.56
$PhCH_2SO_2Cl$	Et_3N	*p*-toluidine	*i*-PrOH	71	29	0.40
$PhCH_2SO_2Cl$	pyridine	*p*-toluidine	*i*-PrOH	50	50	1.0

section D. The results were also similar, being 0.49 and 0.61, respectively. We may conclude tentatively that sulfene itself reacts like phenylsulfene.

When pyridine was used instead of triethylamine, the rate ratio drops from 0.61 to 0.41. The reason for this change is not clear. However, it is evident that the ratio depends to a certain extent on the nature of the tertiary amine.

Two experiments were done with diethylamine and *p*-toluidine traps, one using the usual amount of triethylamine, the other using no triethylamine. The results were quite different, the trapping rate ratios being 3.0 and 15, respectively. This is a rather dramatic demonstration that the nature of the base, or its concentration, influences the outcome of the competition. Both triethylamine and diethylamine are known to give sulfenes with phenylmethanesulfonyl chloride (2).

2. *Experiments with Alcohols*

Alcohols are of course weaker bases than amines, and may be expected to react much slower with sulfenes than amines do. The experiments listed in Table VI indicate that while this is qualitatively the case in some experiments, other experiments are more complex.

The experiments with triethylamine, *p*-toluidine, and

phenol both give results substantially in favor of phenol. This may be explained by considering that phenol probably dissociates in the presence of the strong base, triethylamine. The phenoxide anion, like the sulfonamide anions referred to in section D, is apparently an efficient trap towards both sulfene and phenylsulfene.

When the weaker base pyridine is used instead of triethylamine in the above experiments, *p*-toluidine reacts faster by roughly a factor of 2. Pyridine is apparently not a strong enough base to dissociate phenol to any extent. This is good evidence that phenoxide is responsible for the high yield of ester when triethylamine is used.

A rate ratio similar to the above experiment was obtained in an experiment with phenylmethanesulfonyl chloride, triethylamine, *p*-toluidine and isopropyl alcohol. However, an anomalous result was obtained when the base was pyridine instead of triethylamine. Equal amounts of amide and ester were obtained with pyridine, although triethylamine gave more than twice as much amide. The reason for this result is not known.

3. Competition Reaction with Piperidine and Water

An experiment was carried out with methanesulfonyl chloride, piperidine, and a 9 fold (based on the piperidine) excess of water, in dimethoxyethane solvent. The experimental

conditions were similar to those of the perexchange experiments (see Part III). The experiment was done to demonstrate that the sulfene produced would be efficiently trapped by the amine in spite of the much greater concentration of water. Piperidine was chosen as the amine because it is a secondary amine, and has structural and chemical similarity to quinuclidine.

The crude methanesulfonpiperidide isolated from the reaction mixture accounted for 98% of the product. No attempt was made to isolate the sulfonic acid. Therefore the trapping rate ratio must be calculated by assuming that less than 2% of the product was the sulfonic acid. When the factor of 9 is introduced, the trapping rate ratio may be estimated to be at least 450 : 1 in favor of piperidine.

F. Conclusions

The competition reactions described in this chapter allow the following conclusions to be drawn.

1. Rate ratios are consistently low (except in the piperidine and water experiment). This suggests that sulfenes are highly reactive species, with only small activation energies separating them from the products.

2. When pairs of hard and soft traps are used, the

sulfene reacts fastest with the hard trap. This is evidence for a hard acid nature for sulfenes, and suggests that a comparison with sulfur trioxide (also a hard acid) is useful.

3. In general, stronger bases react faster with sulfenes than weaker bases. This was found to be true for aniline derivatives and diethylamine, and usually for alcohols.

4. It was found that the outcome of the experiments was sensitive to the exact experimental conditions, particularly the nature and concentration of the base.

PART III

PEREXCHANGE EXPERIMENTS

A. Introduction

Sulfenes are very reactive intermediates, and have never been isolated. Therefore all evidence for their existence is circumstantial (see the General Introduction and (1) for a summary of the evidence). Some of the most convincing evidence we have is the observation by King and Durst that alkanesulfonyl chlorides exchange one α-hydrogen when reacted with bases in the presence of deuterium oxide, methanol-*d*, or other deuterated traps (2). Similar experiments carried out since then (see Lee (15) and this thesis) have confirmed these conclusions and extended their generality. A summary of the experiments may be found in Table VII. Essentially the same conclusions are obtained for a wide variety of sulfonyl chlorides and diverse bases (primary, secondary, tertiary, aromatic, and inorganic).

Similar results were obtained by Truce and Campbell (3), who generated sulfenes from alkanesulfonyl chlorides, methanesulfonyl bromide, and methanesulfonic anhydride with

TABLE VII

Summary of some exchange experiments in which sulfonyl chlorides are reacted with bases in the presence of various traps.

Sulfonyl Chloride	Base	Trap	Product[a]
CH_3SO_2Cl	$BuND_2$	-	20.2% CH_3; 79.8% CH_2D[b]
CH_3SO_2Cl	pyridine	D_2O	.947 D[c]
CH_3SO_2Cl	Et_3N	D_2O	.72 D
CH_3SO_2Cl	Et_3N	$PhND_2$	.955 D[c]
CH_3SO_2Cl	Bu_3N	D_2O	6% CH_3; 94% CH_2D[b]
$CH_3CH_2SO_2Cl$	Et_3N	D_2O	.93 D
$PhCD_2SO_2Cl$	$PhNH_2$	-	1.06 D
$PhCH_2SO_2Cl$	Et_2NH	-	1.05 D
$PhCH_2SO_2Cl$	pyridine	D_2O	"one" D
$PhCH_2SO_2Cl$	Et_3N	D_2O	.977 D
$PhCH_2SO_2Cl$	Et_3N	MeOD	.974 D
$PhCD_2SO_2Cl$	Et_3N	MeOH	1.026 D[d]
$PhCH_2SO_2Cl$	Et_3N	*i*-PrOH	.909 D
$PhCH_2SO_2Cl$	NaOD	D_2O	"one" D
p-$NO_2C_6H_4CH_2SO_2Cl$	Et_3N	D_2O	.834 D[c]
$PhCH_2CH_2SO_2Cl$	Et_3N	D_2O	.94 D

a. Composition of product. From ref. 2 except where noted.

b. This work.

c. Ref. 15.

d. Ref. 20.

triethylamine in the presence of deuterated traps. Considerably less monodeuteration was reported than in Table VII, the remainder being unexchanged. The authors accounted for the unexchanged product by postulating an S_N2 displacement on sulfur by base, followed by a displacement by the trap. There is good evidence, however, that no displacement occurs (see Part IV B), and the results are readily explained by isotopic dilution of the available deuteron pool by protons from the methanesulfonyl chloride. Both studies in fact reported some unexchanged product. The most significant fact is that both specifically excluded the possibility of any *perexchanged* (di- or tri-exchanged) product.

In certain special instances some evidence of exchange beyond monodeuteration was obtained. Durst reported that stilbene, produced from the reaction of phenylmethane-d_2-sulfonyl chloride and triethylamine in the presence of triethylammonium chloride, contained 0.80 olefinic deuterons, whereas 2 would be expected. The result was rationalized by postulating addition of the elements of HCl to phenylsulfene to give exchanged starting material (20). A similar mechanism has been proposed to explain the appearance of perexchanged sulfonyl fluoride in Part II B of this thesis.

Except for such special circumstances as the above, perexchange at the α-position in sulfene products appears to be unknown. Evidence will now be presented that extensive perexchange may be observed under "ordinary" conditions if the

appropriate tertiary bases are used.

B. Results

In the course of an examination of the reactions of certain unhindered amines with methanesulfonyl chloride, it was decided to confirm the intermediacy of sulfene by carrying out an exchange experiment. The amine was dissolved with deuterium oxide in dimethoxyethane, and the solution was added to a solution of methanesulfonyl chloride in the same solvent. The product, a salt of methanesulfonic acid, was converted to the sulfonyl chloride to facilitate analysis. When quinuclidine was used as base, the product was found to be extensively exchanged. The major product (63 mole %) was methane-d_3-sulfonyl chloride, as shown by the mass spectrum. Similar perexchange was observed for the bases 1,4-diazabicyclo[2,2,2]octane (DABCO) and trimethylamine.

The experiment above was repeated (using the same reaction conditions) for *N*-methyldiethylamine, triethylamine, and tributylamine. In each of these cases, the results were close to conventional monodeuteration. *N,N*-dimethylethylamine gave intermediate results. The experiments and results are given in Table VIII.

Experiments were done with DABCO and trimethylamine in which less than an excess of amine was used. Starting material was recovered and examined for exchange. No evidence of sig-

TABLE VIII

Results of exchange experiments with methanesulfonyl chloride, tertiary amines, and deuterium oxide in dimethoxyethane.

Amine	Composition (mole %)[a]				Atoms of D[c]
	CH_3	CH_2D	CHD_2	CD_3	
Quinuclidine	1.8	13.1	21.9	63.1	2.47
DABCO	1.3	16.1	22.8	59.8	2.41[d]
Me_3N	1.8	25.6	24.7	48.0	2.19
Me_2EtN	4.8	71.4	17.6	6.2	1.25
$MeEt_2N$	4.8	92.0	2.5	0.8	.99
Et_3N	9.6	89.8	0.5	0	.91
Bu_3N[b]	6	94	-	-	.94

a. Obtained by mass spectrometry, except as noted.

b. Obtained by n.m.r. spectroscopy.

c. Calculated from the mass spectrometry results.

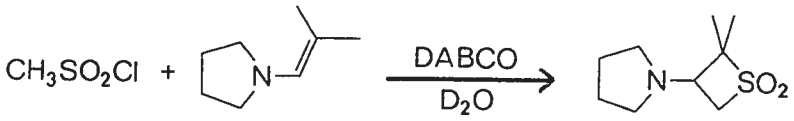
d. A Nemeth deuterium analysis gave 77.50 atom % excess deuterium. This corresponds to 2.32 atoms of D in the methyl group.

nificant exchange was found; in the DABCO experiment, less than 0.5 mole % (close to experimental error) of monodeuterated sulfonyl chloride was detected.

In order to demonstrate the generality of these experiments, an experiment was done under the same conditions using ethanesulfonyl chloride and DABCO. The product was analysed as ethanesulfonyl chloride, and was found to be 5.5% $CH_3CH_2SO_2Cl$, 81.4% CH_3CHDSO_2Cl, and 13.1% $CH_3CD_2SO_2Cl$. The amount of exchange beyond the monodeuterated stage was significant, although it is not as extensive as in the methanesulfonyl chloride experiment.

In another experiment, the reaction of methanesulfonyl chloride and DABCO in the presence of methanol-*d* was examined. The product was the methyl ester, and the sulfonyl methyl group contained 76 atom % D. This is similar to the result obtained from the experiment using deuterium oxide as a trap.

Perexchange was also observed in an experiment with an enamine. When a solution of DABCO, deuterium oxide, and



the enamine was added to a solution of methanesulfonyl chloride, the product obtained was found to have about 0.75 D at the position α to the sulfone group. The product did not exchange under reaction conditions. The yield in this experiment was

44%, as opposed to 52% when deuterium oxide was not included.

C. Discussion

The foregoing results are rather surprising, in view of the fact that such apparently good evidence has been gathered for the intermediacy of sulfenes in the reaction of alkanesulfonyl chlorides with tertiary amines (see also the Introduction to Part IV). One possible explanation of the results appears to be that unhindered amines may be capable of doing a direct displacement on the sulfur atom at a rate comparable to or faster than sulfene formation. The

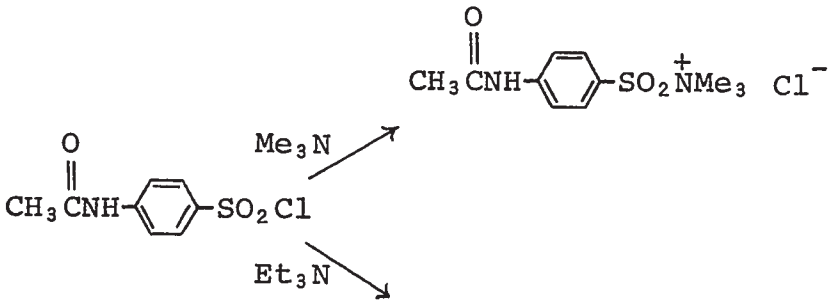
$$R_3N + CH_3SO_2Cl \longrightarrow CH_3SO_2\overset{+}{N}R_3\ Cl^-$$

product of such a displacement would be a sulfonammonium ion. This mechanism is similar to the one proposed by Truce and Campbell (3). The sulfonammonium ion may be expected to be acidic, and exchange with deuterium oxide would occur. More hindered amines would not display this behaviour, on account of serious steric interaction with the sulfonyl group; an elimination of HCl would occur almost exclusively, leading to monoexchange.

There is evidence in the literature that aromatic sulfonyl chlorides behave differently towards unhindered and hindered amines, and that the product of these reactions are

sulfonammonium ions. As early as 1910, Vorländer reported the isolation of an "adduct" of trimethylamine and benzenesulfonyl chloride. A sulfonammonium ion structure was

proposed for the salt-like material (24). It soon became apparent that some amines, such as dimethylethylamine and dimethylbenzyl amine, gave similar salt-like adducts, whereas triethylamine did not (25, 26). Similar observations were made when the action of trimethylamine and triethylamine on *p*-acetamidobenzenesulfonyl chloride were compared. Trimethylamine produced an adduct in an exothermic reaction, whereas triethylamine was unreactive (27).



only starting material isolated

This behaviour is not limited to aromatic sulfonyl chlorides. When methanesulfonyl chloride in acetonitrile was treated at -20° with trimethylamine, an adduct formulated as $CH_3SO_2\overset{-}{C}HSO_2\overset{+}{N}Me_3$ was obtained. This zwitterion is similar in structure to a sulfonammonium ion. It was possible to isolate

the adduct; it was stable to air at room temperature, and tolerated brief contact with water. Under the same conditions, triethylamine produced no detectable adduct. Only at -40° was an adduct obtained, and it could not be studied satisfactorily on account of its instability (1, 7).

In spite of the attractiveness of the S_N2 mechanism, there is evidence that this explanation is not satisfactory. If unhindered tertiary amines do an S_N2 displacement on sulfur, the same mechanism would be expected for primary amines. Thus butylamine-d_2 should produce the sulfonammonium ion shown,

$$CH_3SO_2Cl + BuND_2 \longrightarrow CH_3SO_2\overset{+}{N}D_2Bu\ Cl^-$$

which would be expected to lose one of the very acidic deuterons on the nitrogen much faster than one of the methyl hydrogens. The result would be an unexchanged product. When the experiment was done, the product was found to be 80 mole % monodeuterated, indicating that at least 80% of the reaction went via a sulfene. Similar results have been reported for the reaction of both aniline and diethylamine with phenylmethanesulfonyl chloride (see Table VII).

Further evidence against the displacement mechanism was obtained from rate studies. If the unhindered amines react primarily by means of a displacement reaction, this reaction must be considerably faster than sulfene formation. Therefore the rate of reaction should be faster for unhindered

amines than for hindered amines of similar basicity, just as was observed for the aromatic examples cited. Yet no large change in rate was observed (see Part IV B). In fact the second-order rate constants for the reaction of trimethylamine and triethylamine with methanesulfonyl chloride were 2.40×10^{-2} and 2.99×10^{-2}, respectively.

This argument suggests that all amines, hindered or unhindered, react in the same way in the rate-determining step. It might in principle be argued that all amines have an S_N2 displacement reaction in common as the initial step. Exchange would occur only in the case of the less hindered amines, which form relatively stable sulfonammonium ions. The more hindered amines would instead eliminate H^+ and the amine, forming sulfene. But this mechanism would also demand an important dependence of reaction rate on the stereochemistry of the amine. In Part IV B, unambiguous evidence is presented showing that the rate of reaction depends *only on the basic strength of the amine*, as measured in dimethoxyethane using an indicator as reference acid. There is no detectable dependence on stereochemistry, as is amply demonstrated by the fact that diisopropylethylamine reacts rapidly with methanesulfonyl chloride. Diisopropylethylamine is known to be a very hindered amine, and is a very poor base towards hindered electrophiles (28). It is extremely unlikely that this base could do a displacement on the sulfonyl group at a rate comparable to that of the unhindered amines. The rate

study makes it necessary to conclude that the initial step for all amines studied (including both unhindered and hindered) is an abstraction of the α-hydrogen, attended by loss of chloride, to form a sulfene. The experiment with DABCO, methanesulfonyl chloride, and an enamine mentioned earlier demonstrated that sulfene was present in the reaction mixture. Since the initial step is sulfene formation, and the starting material is known not to exchange before reacting, whatever exchange occurs must take place after sulfene formation.

It is possible to exclude readdition of the elements of HCl to the sulfene as the exchange mechanism. This explanation was used by Durst to explain perexchanged stilbene, and in Part II B of this thesis to explain perexchanged sulfonyl fluoride. In the present experiment this can be excluded since starting material was only negligibly exchanged.

The observed exchange cannot be due to reversible protonation or deprotonation of sulfene itself (to form $CH_3\text{-}SO_2^+$ or $\bar{C}H\text{=}SO_2$) since the rate of this exchange would be expected to be dependent on the basicity, rather than the stereochemistry, of the amine. For the same reason exchange of the sulfonate product is an unsatisfactory explanation. (The sulfonate does not appear to exchange readily under rather drastic conditions. When heated for 30 min at 90° in a solution of potassium hydroxide in deuterium oxide, no exchange could be detected by n.m.r.)

The most likely explanation is that sulfene, once

formed, is able to trap tertiary amines, forming a zwitterion. Reaction with the deuterium pool will produce the deuterated sulfonammonium ion, as shown in the scheme. If the amine

$$CH_2{=}SO_2 + NR_3 \longrightarrow \overset{-}{C}H_2\text{-}SO_2\overset{+}{N}R_3$$

$$\overset{-}{C}H_2\text{-}SO_2\overset{+}{N}R_3 \xrightarrow{D^+} CH_2DSO_2\overset{+}{N}R_3$$

is unhindered, the zwitterion and sulfonammonium ion will be relatively stable, as already explained. Exchange will proceed readily by the above mechanism (it is assumed to be reversible). For the hindered amines, the lifetimes of the above species will be much shorter, and reaction of sulfene with deuterium oxide will be faster than the exchange mechanism.

For the above mechanism to hold, sulfene must be capable of trapping the amine much more efficiently than deuterium oxide. (The experiments were done with much more deuterium oxide than tertiary amine - the molar ratio was usually more than 10 : 1.) An experiment was done under approximately the same conditions as the perexchange experiments, except that piperidine, a secondary amine, was used (see Part II E for a full description). It was found that a very good crude yield (98%) of the piperidide was obtained. This result is strong evidence that the sulfene, once formed, is able to react very quickly with amines, even though a much larger amount of water may be present.

In order to demonstrate that an exchanged sulfene exists in the reaction mixture, the experiment with DABCO, deuterium oxide, and enamine already mentioned under Results was done. The product (sulfene-enamine adduct) was exchanged, thus indicating that the sulfene was able to exchange reversibly with the deuterium oxide without becoming trapped by it.

The proposed scheme for the reaction of sulfene with tertiary amine and trapping agent is shown in Fig. II. If the scheme is an accurate representation, quantitative agreement would be expected between calculations based on this scheme and the experimental results. The rate constants for the reactions shown are of course not known, but some reasonable guesses about their relative magnitude may be made. The approximations and some other assumptions to help solve the complex reaction scheme are set forth as follows:

1. It is assumed that all of the sulfene (A) is initially trapped by the tertiary amine.
2. A rapid equilibrium (K) is assumed between A and the zwitterion (B).
3. The trapping agent is assumed to react only with A.
4. The active deuterium pool is assumed to contain no protium. Therefore reactions which in principle are reversible may be regarded as being irreversible.

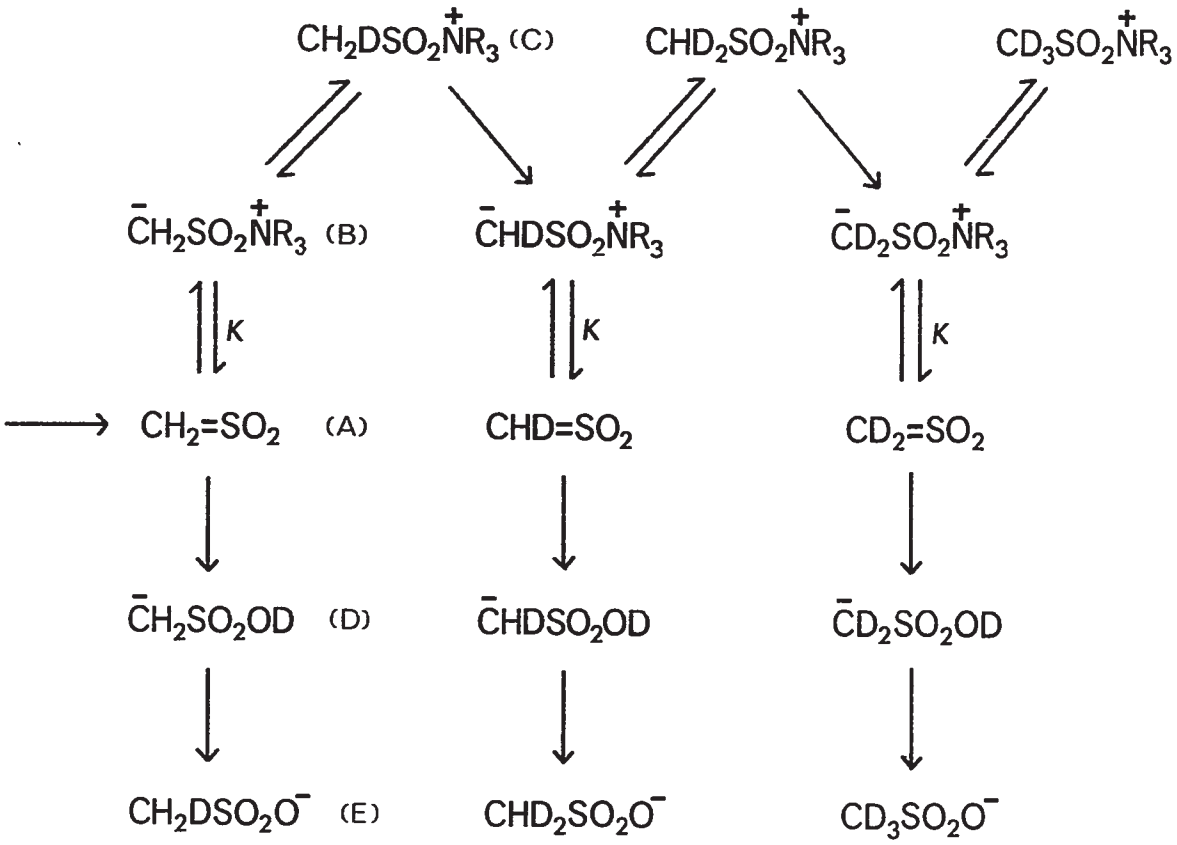


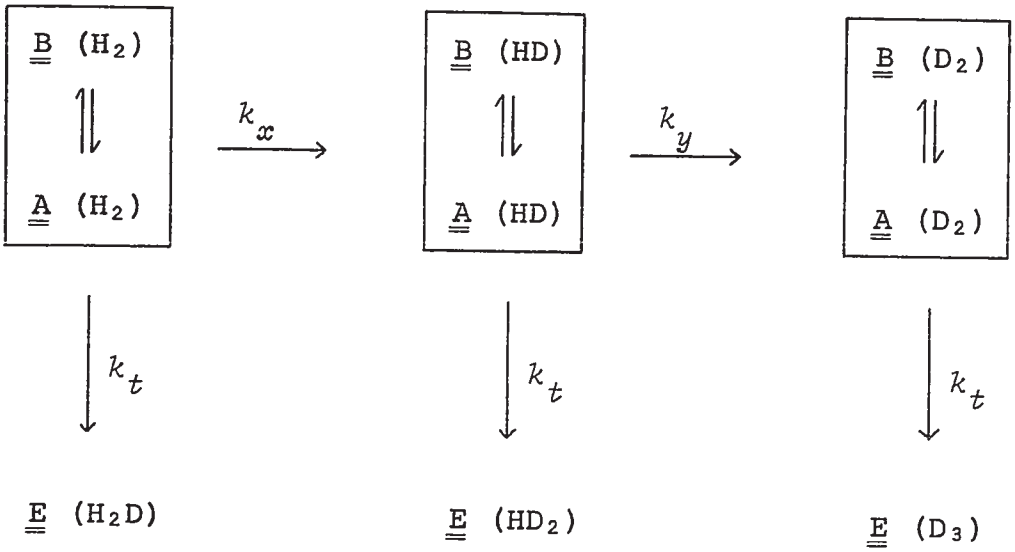
Fig. II. Proposed mechanism to explain exchanged sulfene products.

5. Deuterium isotope effects are ignored. (See Part IV C - usually $k_H/k_D = \sim 1$).

6. The role of $\underline{\underline{C}}$ as an intermediate need not be explicitly considered, and an overall rate from $\underline{\underline{B}}$ (H_2) to $\underline{\underline{B}}$ (HD) and $\underline{\underline{B}}$ (HD) to $\underline{\underline{B}}$ (D_2) may be assumed.

7. Many of the rates will be dependent on the nature of the base, ionic strength, concentration of acidic species, etc. Rather than considering these factors separately, a factor R will be defined to include all of these things (see definition below). R is assumed to be constant for a given amine.

The above are felt to be quite reasonable assumptions for a semi-quantitative test of the reaction mechanism. They allow the setting up of a simplified reaction scheme, as follows:



The overall rate of reaction from $\underline{\underline{B}}$ (H_2) to $\underline{\underline{B}}$ (HD) and $\underline{\underline{B}}$ (HD) to $\underline{\underline{B}}$ (D_2) is k_x and k_y, and the overall rate of formation of product is k_t. From Fig. II, it may be seen that $k_x = 2\,k_y$, since the rate of the exchange reaction depends on the number of H atoms (as opposed to D) available for abstraction. Since $\underline{\underline{C}}$ (H_2D) has two H and $\underline{\underline{C}}$ (HD_2) only one, k_x will be twice as fast as k_y. The ratio of the rate of exchange to the rate of trapping may be defined as

$$\frac{k_x}{k_t} = 2R \text{ and } \frac{k_y}{k_t} = R.$$

The ratio of $\underline{\underline{E}}$ (D_3) to $\underline{\underline{E}}$ (HD_2) in the product will be

$$\frac{D_3}{HD_2} = \frac{k_y}{k_t} = R.$$

The ratio of $\underline{\underline{E}}$ (D_3) + $\underline{\underline{E}}$ (HD_2) to $\underline{\underline{E}}$ (H_2D) in the product will be

$$\frac{HD_2 + D_3}{H_2D} = 2R.$$

If the quantities of H_2D, HD_2, and D_3 are taken as mole fractions, then $H_2D + HD_2 + D_3 = 1$, and

$$H_2D = \frac{1}{2R + 1}$$

$$HD_2 = \frac{2R}{(2R + 1)(R + 1)}$$

$$D_3 = \frac{2R^2}{(2R + 1)(R + 1)}$$

The mole fractions (in %) of the deuterated species are graphed as a function of R in Fig. III. The value of R may be found simply by determining the experimental value of D_3/HD_2 (see Table VIII). Then R may be used to predict the deuterium distribution. This has been done in Table IX. (Note that the values do not add up to 100%. The difference represents the experimental amount of undeuterated material. This material will be mentioned again later in this chapter.)

The agreement with the experimental values is quite good for quinuclidine and DABCO, and is not bad for trimethylamine. However, the results for dimethylethylamine and methyldiethylamine are seriously out, and triethylamine cannot be checked because D_3 is not known (it is presumed to be undetectable but finite). The reason for the error is likely that for the more hindered amines, the rate of trapping of sulfene by the amine is much slower, so that the rate of trapping by the trapping agent (D_2O) will compete favorably. In these cases assumption 1 no longer holds, and the relationship between $\underline{\underline{A}}$ and $\underline{\underline{B}}$ can no longer be described as an equilibrium. In the limit, the sulfene

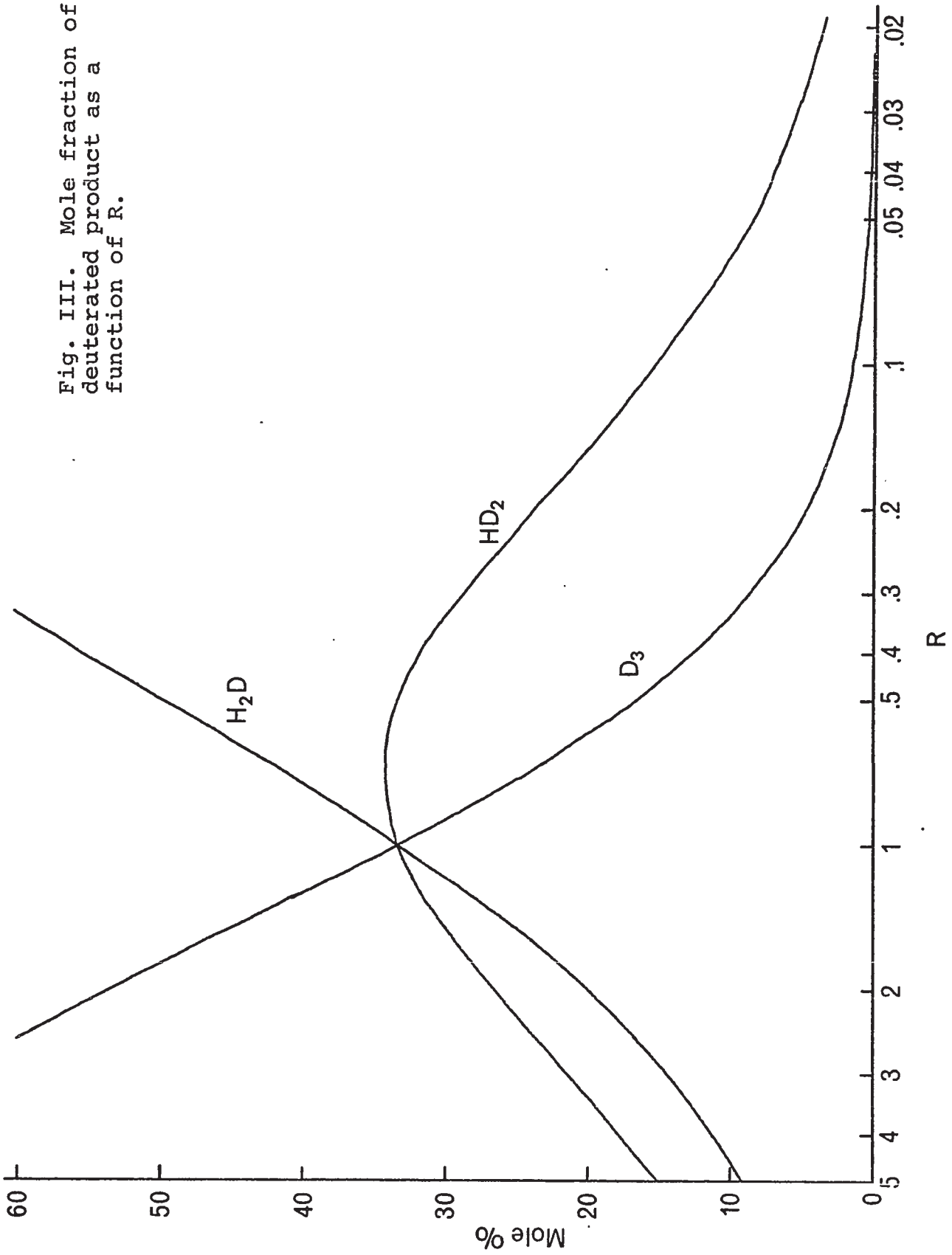


Fig. III. Mole fraction of deuterated product as a function of R.

TABLE IX

Predicted deuterium distribution using the derived values of R.

Amine	R	H_2D	HD_2	D_3	Total
Quinuclidine	2.9	14	21	63	98
DABCO	2.6	16	23	60	99
Me_3N	2.0	20	26	52	98
Et_2EtN	0.35	56	29	10	95
$MeEt_2N$	0.32	58	28	9	95
Et_3N	0.003[a]	90	.5	-	91

a. The value of R for triethylamine was chosen to give the best fit with the experimental results.

traps only deuterium oxide, and monodeuteration results. The result for triethylamine is close to monodeuteration, and probably little trapping by the amine takes place under the reaction conditions. Dimethylethylamine and methyldiethylamine give results with considerably more monodeuterated product than predicted by considering R, but with much more HD_2 and D_3 than predicted for complete trapping of deuterium oxide. Therefore, as their stereochemistry suggests, their behaviour seems to be intermediate between the unhindered and the hindered amines.

It is noteworthy that while methanol-*d* gave results much like deuterium oxide, less exchange was observed when ethanesulfonyl chloride was used instead of methanesulfonyl chloride. This result would be expected, since the extra methyl group would make it sterically more difficult for the amine to bond to the sulfonyl group.

In all experiments, there was some evidence of unexchanged product. This material has been observed before, and never satisfactorily explained (2, 20). No doubt a portion of it is due to isotopic dilution of the active deuterium pool with protium, from the sulfonyl chloride as the reaction proceeds, and from other sources.

The above discussion was intended to demonstrate that the proposed mechanism is consistent with the experimental facts as we now know them. It was not the intention to exclude all other mechanisms. In any case, much remains unknown

about the details of sulfene chemistry, especially its reactions with traps of all kinds. Carefully designed experiments are needed to shed light in these areas.

PART IV

THE MECHANISM OF SULFENE FORMATION

A. Introduction

The mechanism of the reaction of alkanesulfonyl chlorides with amines to give intermediate sulfenes has received considerable attention. King and Durst demonstrated that the reaction likely proceeds via a base-induced elimination of the elements of HCl, and that this elimination is likely concerted (2). The reaction was further investigated by Lee, who considered several ways in which the elimination could take place (5, 15). A choice of the most likely mechanism was made on the basis of kinetic and other evidence. It is useful at this point to review briefly these mechanistic possibilities, and the evidence that was used to choose between them.

Five mechanistic schemes were listed, and they were as follows:

(A) Substitution of the chlorine by the tertiary amine, followed by elimination of the proton and the amine (S_N2 plus

E mechanism).

$$RR'CHSO_2Cl + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RR'CHSO_2B^+ + Cl^-$$

$$RR'CHSO_2\overset{+}{B} + B \xrightarrow{k_2} RR'C{=}SO_2 + \overset{+}{B}H + B$$

(a) with a prior equilibrium ($k_{-1} > k_2$)

(b) with k_1 rate-determining ($k_{-1} < k_2$).

(B) Initial base-induced formation of a carbanion, followed by elimination of chloride ion (Elcb mechanism)

$$RR'CHSO_2Cl + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RR'\overset{-}{C}SO_2Cl + \overset{+}{B}H$$

$$RR'\overset{-}{C}SO_2Cl \xrightarrow{k_2} RR'C{=}SO_2 + Cl^-$$

(a) with a prior equilibrium ($k_{-1} > k_2$)

(b) with k_1 rate-determining ($k_{-1} < k_2$).

(C) A concerted elimination of both proton and chloride ion (E_2 mechanism).

$$RR'CHSO_2Cl + B \xrightarrow{k} RR'C{=}SO_2 + \overset{+}{B}H + Cl^-$$

For a detailed discussion of these mechanisms with a derivation of the rate expressions for each, the reader is referred to the original work (15).

It is possible to eliminate one of the mechanisms immediately. Mechanism B(a) features a prior equilibrium which would rapidly exchange the α-hydrogens. King and Durst have shown that such exchange does not occur (2).

Another possibility may be eliminated from a consideration of the reaction kinetics. In all cases examined, the reactions are first order in sulfonyl chloride and first order in tertiary amine (5). Since mechanism A(a) is predicted to be second order in amine, it may be eliminated.

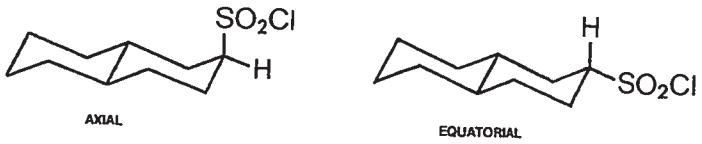
This leaves three mechanisms to choose from. The main difference between them is that mechanism A(b) involves attack of the amine at sulfur, whereas mechanisms B(b) and C involve abstraction of an α-hydrogen by the amine. Mechanisms B(b) and C are variations of the same basic scheme - in B(b) the loss of chloride (after the abstraction of the proton) is merely fast, whereas in C it is immediate (*i.e.* concerted).

Some evidence is available to discriminate amongst these three possibilities:

1. Stereochemical Evidence

In mechanism A(b), the rate-determining step involves

the close approach of the amine to the sulfonyl group. The space around the sulfur atom will therefore become quite cluttered. On the other hand, no such cluttering occurs in mechanisms B(b) and C. In fact the loss of chloride and formation of sulfene may reduce the size of the functional group. Thus the decalin sulfonyl chlorides shown were



prepared, and their rates of dehydrohalogenation measured. The axial (hindered) sulfonyl chloride reacted 71 times faster than the equatorial isomer. This was interpreted as evidence that a certain amount of steric relief was obtained in the axial case, and excludes mechanism A(a). Mechanism C appears to fit the evidence best, but B(b) cannot be excluded (5).

2. Rate Studies

Second-order rate constants were determined for the reaction of several sulfonyl chlorides with triethylamine at -25°. See Table X. The relative rates vary over quite a range, and were explained by considering the effect of the α-phenyl group on the acidity of the α-hydrogen, the inductive effects of the α-alkyl groups, and the stereochemistry of the sulfonyl chlorides. The reaction rates were shown to be con-

sistent with a rate-determining deprotonation step, and are not readily reconciled with A(b) (15).

TABLE X

Second-order rate constants for the reaction of sulfonyl chlorides with triethylamine at -25° (15).

Sulfonyl Chloride	Relative Rate
$PhCH_2SO_2Cl$	1000
CH_3SO_2Cl	1
$CH_3CH_2SO_2Cl$	1/14
$C_6H_{11}SO_2Cl$	1/480

3. Hammett Plot

Rate studies were done on the reaction of aryl-substituted phenylmethanesulfonyl chlorides with pyridine at 20°C. A plot of the logarithms of the rate constants vs. σ^- produced a straight line with a slope of $\rho = 2.35$ (5). This indicates a δ^- on the α-carbon in the transition state (relative to starting material), and appears to be consistent with both B(b) and C mechanisms.

4. Rates of Exchange of Sulfonyl Compounds

It was observed that compounds such as sulfones, sulfonamides, and sulfonate esters exchange the protons α to the sulfonyl group at a rate of $\sim 10^8$ times slower than sulfene formation from the corresponding sulfonyl chloride. This was taken as indicating a difference in mechanism, and was assumed to support mechanism C as opposed to B(b) (5). Mechanism A(b) does not appear to be excluded by this evidence.

5. Deuterium Isotope Effect

The fraction k_H/k_D was found to be 2.0, 2.6, and 4.1 for the reaction of phenylmethanesulfonyl chloride with pyridine, triethylamine, and sodium hydroxide, respectively (19, 5). These values are moderate, and are consistent with a transition state in which the α-proton is being abstracted by the amine, with proton transfer to the amine nearly complete. This evidence supports mechanism B(b) and C.

The evidence listed above taken together tends to support a concerted dehydrohalogenation (mechanism C), and tends to exclude mechanism A(b). Some doubt about the mechanism appears to remain, however. The following points are reminders that the mechanism has not been proved, and that more evidence is needed:

In most cases the generality of the evidence has not been demonstrated. For instance, while there appears to be good evidence that the decalin sulfonyl chlorides do a concerted elimination, it is not certain whether this conclusion may be extended to other sulfonyl chlorides. Similarly, it is not known whether the conclusions drawn from experiments with phenylmethanesulfonyl chloride are equally valid for other sulfonyl chlorides.

Although exchange experiments are considered very good evidence for sulfene intermediacy (see the Introduction to Part III and Table VII), these experiments always produce a greater or lesser amount of *unexchanged* product. For example, King and Durst found 28 mole % of unexchanged product in the reaction of methanesulfonyl chloride with triethylamine (in dioxane at -5°C) in the presence of deuterium oxide (2). Substantial quantities of unexchanged products were reported by Truce and Campbell (3) (but see comment on p. 31 of this thesis). Both papers suggested that the source of this material might be a direct displacement mechanism*. This displacement would necessarily be a displacement by the tertiary amine, forming a sulfonammonium ion, since the trap (*e.g.* methanol-*d*) will not react by itself under reaction conditions. See

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* Good independent evidence for a direct displacement by fluoride ion on a sulfonyl chloride has been obtained in Part II B of this thesis. The reaction is very fast, and is faster than the elimination reaction that produces the sulfene, under some conditions.

Part III C for a discussion of this mechanism. Without further evidence, it cannot be concluded with certainty whether the direct displacement reaction contributes to a small but noticeable extent, to a large extent, or not at all.

A series of experiments with unhindered tertiary amines (quinuclidine, DABCO, and trimethylamine) was described in Part III of this thesis. These amines were able to produce extensively perexchanged products when used to generate sulfenes in the presence of deuterated traps. At first this seemed to be excellent evidence for a direct displacement reaction, at least for unhindered amines. The resultant sulfonammonium ions would then be responsible for the observed exchange. It was primarily to settle the question of the mechanism of the perexchange reaction that the experiments in the next section were done.

B. Correlation of the Rate of Reaction with the Basic Strength of the Amine

As explained in the introduction, the most likely mechanism for the dehydrohalogenation of alkanesulfonyl chlorides is an abstraction of the α-hydrogen by the amine, accompanied by loss of chloride ion. The expectation is that a strong tertiary amine will react faster than a weak one, and that a linear relationship might exist between basic strength and rate of reaction. Some evidence that this

was at least qualitatively true was obtained by King and Lee, who found a rate difference of 10^5 between the reactions of triethylamine and pyridine with methanesulfonyl chloride (5).

The relationship would not be expected to be as simple if the mechanism is the direct displacement reaction. The bulky sulfonyl group should severely hinder the attack of sterically hindered amines. A number of kinetic studies of aromatic sulfonyl chlorides with nucleophiles have appeared in the literature (29); these sulfonyl chlorides cannot form sulfenes, and are believed to undergo displacement reactions. Unfortunately there appears to be no report of the rates of reaction of tertiary amines with aromatic sulfonyl chlorides. Qualitative experiments, however, indicated that hindered amines react much more slowly than unhindered ones* (see also the discussion and references on p. 38). Rate studies of alkanesulfonyl chlorides should quickly reveal what the first step of the mechanism is.

Results and Discussion

The rates of reaction of a number of tertiary alkylamines

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* Approximately 200 mg each of DABCO, triethylamine, and diisopropylethylamine were added to different solutions of ∿200 mg of benzenesulfonyl chloride in 15 ml of anhydrous ether. The DABCO solution produced a white precipitate immediately and the triethylamine after 10 min. No reaction was noted for diisopropylethylamine after 48 h.

with methanesulfonyl chloride were measured, using the method described by Lee (15). Kinetics were done at -25° and +20°C in dimethoxyethane. No traps were used. The reaction was followed by titrating for chloride ion with silver nitrate solution. An excess of the amine (20 fold) was used, so that pseudo-first-order kinetics could be observed. All runs produced good straight lines in a plot of log concentration of sulfonyl chloride against time, and k_{obs} was determined by multiplying the slope by 2.303. The second-order rate constant k_2 was derived from k_{obs} by dividing by the concentration of the amine. The results may be found in Table XI. The pK_a's of the amines are also given.

When the logarithms of the second-order rate constants were plotted against the pK's of the amines, a Brönsted plot (34) was obtained. See Fig. IV. As the graph indicates, a good relation was not obtained. A closer inspection revealed that the distribution was not random, however. There appears to be a general increase of rate (*e.g.* along the dotted line) with increasing pK_a except that bases like quinuclidine and DABCO, which are readily solvated by water (they are deliquescent), are well to the left of the line, and hydrophobic bases like diisopropylethylamine and tributylamine lie to the right of the line. This suggests that the pK_a's reflect serious interactions with water that do not occur to the same extent in dimethoxyethane, with the result that hydrophilic bases have unusually low pK_a's and hydrophobic

TABLE XI

Reaction rates of various tertiary amines with methanesulfonyl chloride in dimethoxyethane at the temperatures indicated.

Base	k_2 (l mole^{-1} sec^{-1}) -25°C	k_2 (l mole^{-1} sec^{-1}) 20°	pK_a Value	pK_a Reference
Quinuclidine	1.41		10.95	30
DABCO[b]	1.68×10^{-1}		8.38[c]	a
Me_3N	2.40×10^{-2}		9.76	31
Me_2EtN	1.84×10^{-2}		9.99	31
Et_2MeN	2.27×10^{-2}		10.29	31
Et_3N	2.97×10^{-2}	0.222	10.65	31
i-Pr_2EtN	4.90×10^{-3}	4.09×10^{-2}	11.29	a
Bu_3N	1.85×10^{-3}	2.17×10^{-2}	10.89	32
	1.04×10^{-4}	1.82×10^{-3}	7.41	33

a. This thesis.

b. The average value for k_2 in the experimental is 3.35×10^{-1}. Because DABCO is bifunctional, this value must be divided by 2 for purposes of comparison with the other amines.

c. The value for pK_a in the experimental is 8.68. It must be reduced by log 2 for comparison with the other amines.

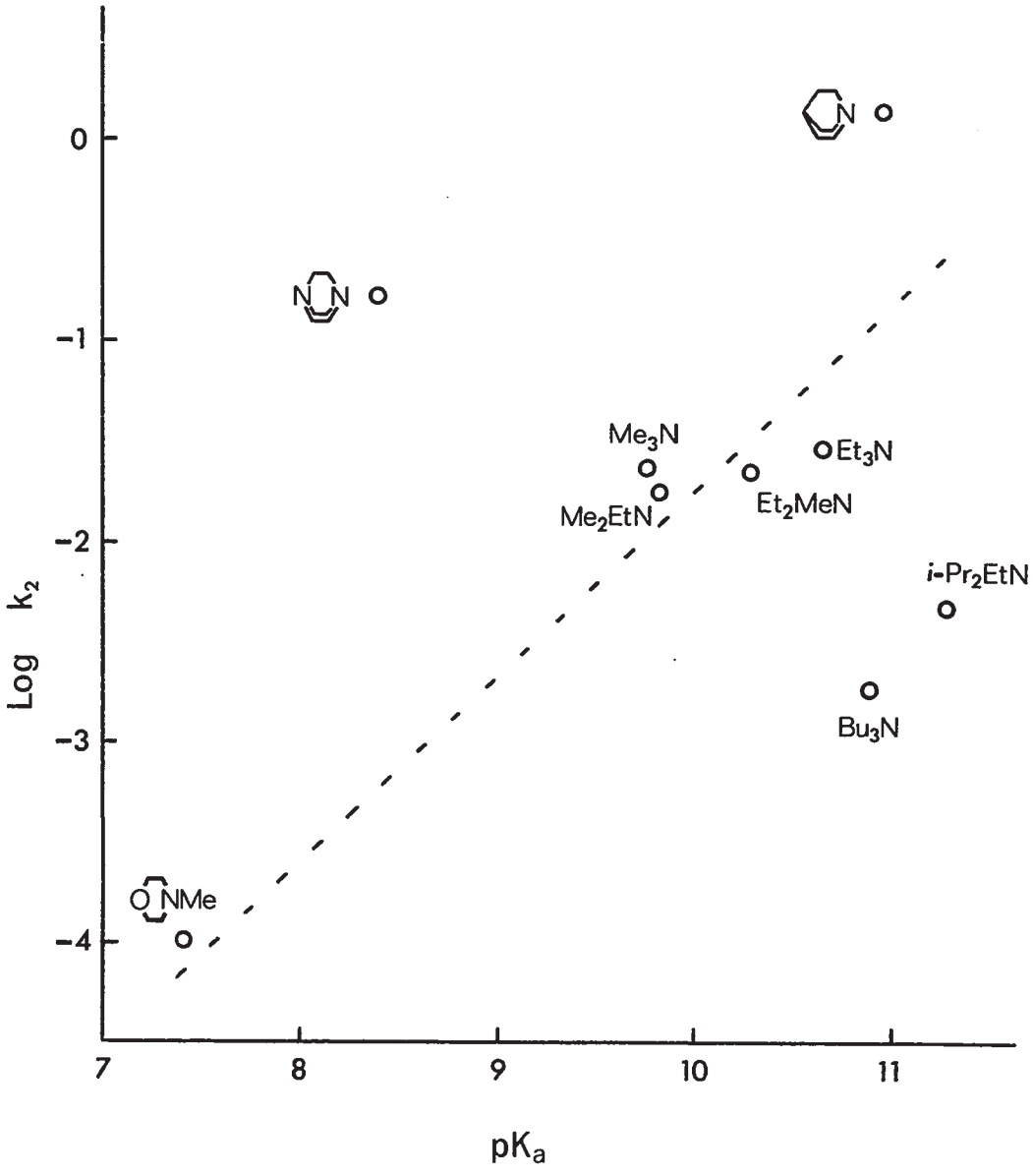

Fig. IV. Brönsted plot, for the reaction of methanesulfonyl chloride with tertiary amines at -25° in dimethoxyethane.

bases high pK_a's, compared to what they would be in non-polar solvents.

In order to resolve this discrepancy, the basic strengths of the amines were determined in dimethoxyethane by using an indicator, 2,4-dinitrophenol, as a reference acid. The method was as described by Bayles and Chetwyn (35 - see also 36 and 37). Known quantities of the amine (B) and the indicator (HA) were dissolved in dimethoxyethane, and the amount of phenoxide anion (A^-) determined spectrophotometrically by measuring the absorbance of the solution in the ultraviolet spectrum. Excellent isosbestic points were obtained in all determinations. The following relation was found to hold:

$$K = \frac{[\overset{+}{B}H \cdots \overset{-}{A}]}{[B]\,[HA]}$$

The equilibria in all cases appeared to involve only the free amine, the free indicator, and a binary complex of the ammonium ion and the phenoxide anion ($\overset{+}{B}H \cdots \overset{-}{A}$). The equilibrium constants K_{DME} and log K_{DME} were calculated, and may be found in Table XII. The values of ΔG are also given, and were calculated from the relation $\Delta G = -RT \ln K_{DME}$.

A comparison of Table XII with Table XI reveals that the relative basic strengths of the amines as measured by log K_{DME} are much different from the relative values of their

TABLE XII

Equilibrium constants and log equilibrium constants for the reaction

$$B + HA \rightleftharpoons [\overset{+}{B}H \cdots \overset{-}{A}]$$

where B is a tertiary amine and HA is 2,4-dinitrophenol. Determined in dimethoxyethane.

B	K_{DME}	log K_{DME}	ΔG (Kcal/mole)
Quinuclidine	2.4×10^5	5.38	-7.28
DABCO[a]	1.8×10^4	4.25	-6.15
Me_3N	1.4×10^4	4.13	-5.60
Me_2EtN	1.0×10^4	4.00	-5.42
Et_3N	1.3×10^4	4.10	-5.55
i-Pr_2EtN	3.1×10^3	3.49	-4.73
Bu_3N	1.6×10^3	3.20	-4.33
	1.7×10^2	2.23	-3.02

a. Since DABCO is bifunctional, the values here are lower by a factor of 2 than in the experimental. This facilitates comparison with the other amines.

aqueous pK_a's. It appears that amines such as diisopropylethylamine owe their high aqueous basicities to their hydrophobic interaction with water (as the free base). On the other hand, hydrophilic bases such as DABCO and quinuclidine tend to have weaker aqueous pK_a's than one would expect from the dimethoxyethane values.

A plot of the log of the second order rate constants (Table XI) at -25° vs log K_{DME} produced a much better relation than before. See Fig. V. An excellent straight line was obtained, with a slope of -1.30.* Another plot on the same figure used log k_2 values determined at 20°C, which is close to the temperature at which the K_{DME}'s were determined. Quinuclidine was found to react too fast for a rate constant to be determined at 20°. While the plot at 20° only has four points, its slope of -1.11 is expected to be more significant than the slope of the low temperature plot.

The rate relationship depicted in Figure V may be stated mathematically as

$$\log k_2 = \beta' \log K_{DME} + C$$

where β' (similar to the Brönsted constant) and C are constants.

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* Only the point for DABCO (which is bifunctional, and may be anomalous for reasons related to this) falls significantly off the line.

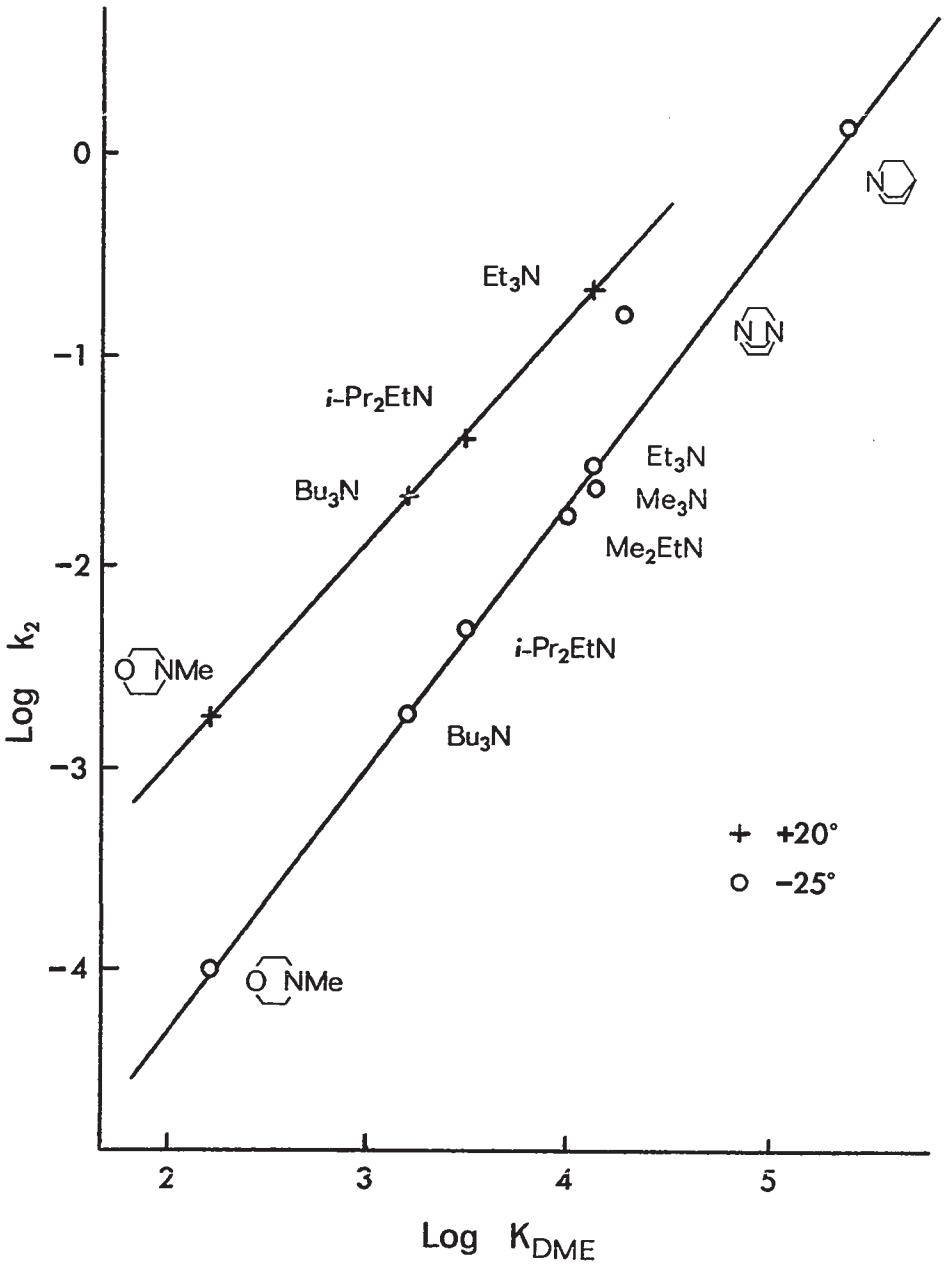

Fig. V. Plot of log k_2 against the basicity of the amines as determined in dimethoxyethane (log K_{DME}).

The relation states that the rate of reaction of a monofunctional aliphatic tertiary amine with methanesulfonyl chloride depends linearly upon the basic strength of the amine, as measured with the reference acid 2,4-dinitrophenol in dimethoxyethane. This is strong evidence that the amine reacts by abstracting a proton from the sulfonyl chloride. It is compelling evidence that the rate-determining step leading to chloride formation is not an S_N2 displacement by the amine on the sulfonyl sulfur atom, since the rate is not influenced in any detectable way by the stereochemistry of the amine.

The foregoing is not meant to imply that there are no stereochemical demands whatsoever on the amine. In fact, stereochemistry probably influences k_2; but there is a parallel effect in K_{DME}, as shown by the linear plot. The only reasonable way to account for this parallelism is to conclude that a similar process is taking place in each reaction; that is, a proton abstraction.

It is useful at this point to examine possible reaction energy profiles, and to select the one that appears to describe the reaction most accurately. The approach that follows is similar to that discussed by Bell, and the reader is referred to it for details (38). In Figure VI, the energy diagram (a) refers to a situation where S^- $(\bar{C}H_2SO_2Cl)$ is a stronger base than B(the amine). Diagrams (b) and (c) show S^- as about equal to B and weaker than B, respectively. The reaction

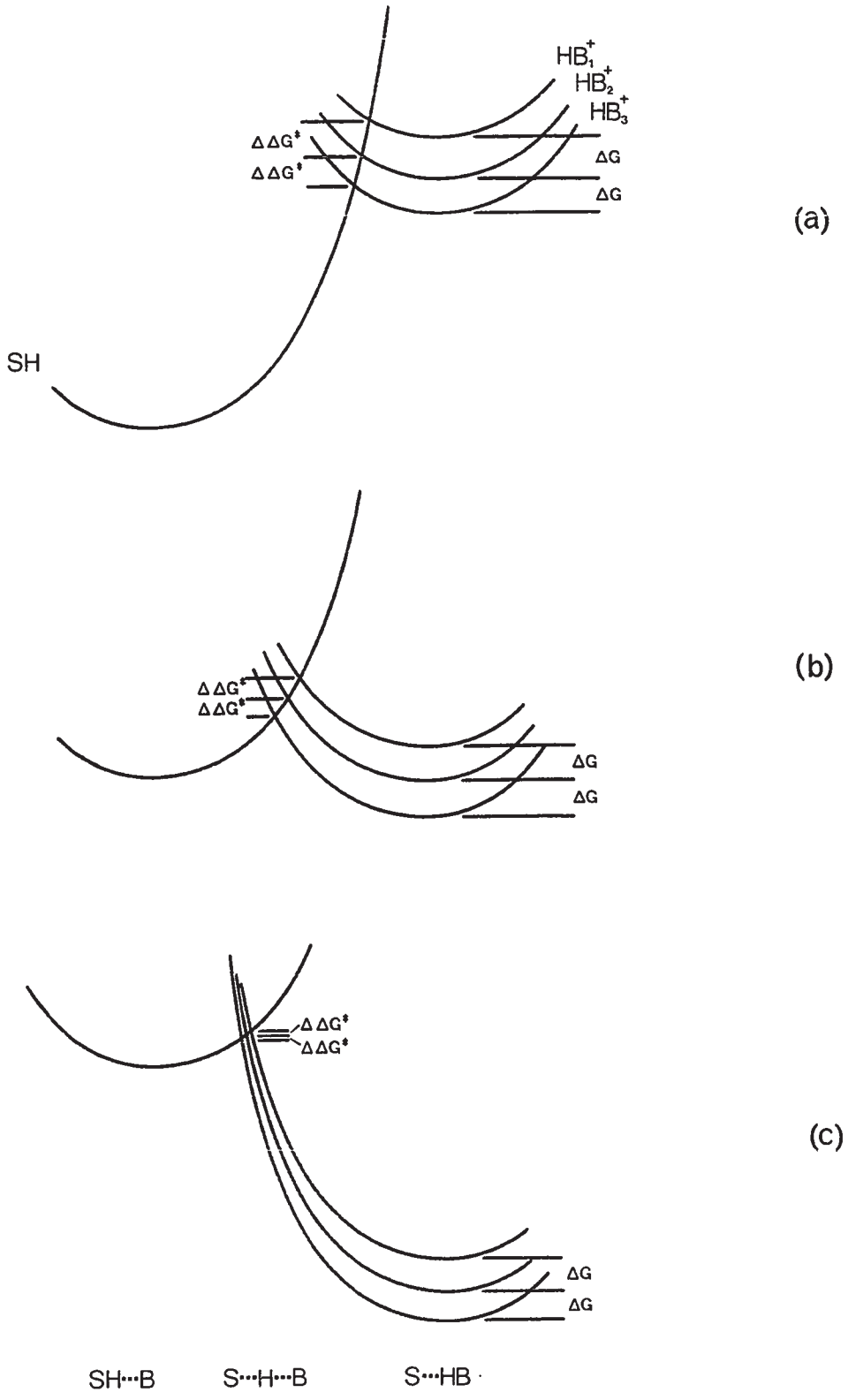

Fig. VI. Reaction energy profiles.

coordinate (abscissa) describes the position of the hydrogen atom, relative to either $\bar{S}$ or B. The transition state is reached approximately where the lines intersect. In (a), $\Delta\Delta G^{\ddagger}$ is about the same in magnitude as ΔG; in (b), $\Delta\Delta G^{\ddagger}$ is about half as big as ΔG; in (c), $\Delta\Delta G^{\ddagger}$ is very small compared to ΔG.

The factor of proportionality relating $\Delta\Delta G^{\ddagger}$ and ΔG is β', the slope of the plot of log k_2 vs. log K_{DME}.

$$\log k_2 = \beta' \log K_{DME} + C$$

$$\Delta \ln k_2 = - \frac{\Delta\Delta G^{\ddagger}}{RT}$$

$$\Delta \ln K_{DME} = - \frac{\Delta G}{RT}$$

Since β' was experimentally found to be -1.11, it is clear that diagram (a) comes closest to describing the reaction. In this scheme, the proton has been almost completely transferred to the amine, and the transition state is more like the product than the starting materials.

Normally, at least in aqueous systems, a slope of more than one would not be expected. This follows if the shapes of the curves in the diagram are all the same. The reason for the high β' may be an error in the values of K_{DME} (and consequently ΔG) for the triethylammonium ions. Since these

values were determined from the reaction of the amines with 2,4-dinitrophenol, the discrepancy may be the assumption that the free energy of the phenoxide is the same in all cases. In fact, this may not be the case, since the free energy may be expected to vary somewhat with the strength of the acid (*i.e.* protonated amine). In addition, the energy of the hydrogen bond must be considered. These considerations probably apply to the sulfonyl chloride as well. A complex picture emerges, and the exact significance of the slope becomes difficult to assess.

Three different reaction schemes consistent with an abstraction of hydrogen by the amine may be envisaged.

1. A rapid equilibrium between the amine and sulfonyl chloride, and a binary complex, followed by a slow loss of chloride.

$$R_3N + CH_3SO_2Cl \underset{}{\overset{K}{\rightleftharpoons}} [R_3\overset{+}{N}\text{-}H\cdots\overset{-}{C}H_2SO_2Cl]$$

$$\text{(slow) } k \Big\downarrow -Cl^-$$

$$R_3\overset{+}{N}HCl^- \quad CH_2{=}SO_2$$

Reversal of the proton abstraction in the first step would not exchange the proton. Exchange would have to occur by loss of the $R_3\overset{+}{H}\text{-}N$ group, and this reaction may proceed quite slowly.

The reaction kinetics would be

$$\text{Rate} = kK[B][S].$$

2. A slow abstraction of hydrogen ion, followed by a rapid loss of chloride.

$$R_3N + CH_3SO_2Cl \xrightarrow[\text{(slow)}]{k_1} [R_3\overset{+}{N}H\cdots\overset{-}{C}H_2SO_2Cl]$$

$$\text{(fast) } k_2 \downarrow \quad -Cl^-$$

$$R_3\overset{+}{N}H\overset{-}{Cl} \qquad CH_2{=}SO_2$$

The reaction kinetics would be

$$\text{Rate} = k_1[B][S].$$

3. A concerted elimination of hydrogen ion and chloride ion.

$$R_3N + CH_3SO_2Cl \xrightarrow{k} R_3\overset{+}{N}H\overset{-}{Cl} \quad CH_2{=}SO_2$$

The reaction kinetics would be

$$\text{Rate} = k[B][S].$$

While for the most part in this section the abstraction of a proton was depicted as giving a species like $\bar{C}H_2SO_2Cl$, this must not be taken as an assumption that the elimination cannot be concerted. The evidence suggests a negative charge (δ^-) on the carbon, and this may apply equally well to a concerted mechanism. All the above reaction schemes are second order in kinetics, and seem to fit the evidence well. On the basis of the experimental evidence in this section, a choice of the mechanisms does not seem possible.

C. The Kinetic Isotope Effect

Further evidence regarding the rate-determining step of the reaction of alkanesulfonyl chlorides with tertiary amines may be gathered by considering the deuterium isotope effect. In general the ratio k_H/k_D may be expected to be high (around 7) for reactions in which the partially abstracted hydrogen is bonded with similar strength to the abstracting base and the substrate, in the transition state. A low deuterium isotope effect may be expected when, in the transition state, hydrogen transfer has just begun (*i.e.* strong bond to the substrate, weak bond to the base), or when hydrogen transfer is nearly complete (*i.e.* weak bond to the substrate, strong to the base)(39).

Some work on the deuterium isotope effect in sulfene

formation has already been done by Peterson (19) and Lee (5), who examined the product of the reaction of phenylmethane-*d*-sulfonyl chloride ($PhCHDSO_2Cl$) with pyridine, triethylamine, and sodium hydroxide in dioxane in the presence of water. The sulfonate product was converted to the sulfonyl chloride to facilitate analysis, and was examined for deuterium content. The ratio of monodeuterated product to nondeuterated product was assumed to be equivalent to the deuterium isotope effect. (This assumption may not be strictly valid, since the formation of strongly associated complexes in non-polar solvents may result in return of the hydrogen (or deuterium) that was removed in the first place. However, the assumption may be sufficiently valid for these purposes.)

The results indicated deuterium isotope effects of 2.0, 2.6, and 4.0 when pyridine, triethylamine, and sodium hydroxide were used as bases, respectively. These values were moderate, and were interpreted as indicating that the hydrogen was not equally bonded to substrate and base in the transition state. The fact that the highest isotope effect was obtained with the strongest base was taken as evidence that hydrogen transfer to the base was almost complete. (This follows from a consideration of the energy diagram - see (15).)

Results and Discussion

The deuterium isotope effect of sulfene formation from methanesulfonyl chloride was studied by measuring the rates of reaction of natural abundance methanesulfonyl chloride and methane-d_3-sulfonyl chloride with a number of bases. Methane-d_3-sulfonyl chloride was prepared by the action of DABCO on natural abundance methanesulfonyl chloride in the presence of deuterium oxide. The product (the sulfonate) contained about 2.4 atoms of deuterium in the methyl group, as shown by conversion to the sulfonyl chloride and analysis by mass spectrometry (see Part III B). Repetition of the above procedure further enriched the methyl group's deuterium content. A third treatment gave a product which was better than 98 atom % D in the methyl group.

The kinetic experiments were carried out at -25° as described in the previous section. The bases used were DABCO, triethylamine, and diisopropylethylamine. See Table XIII.

TABLE XIII

	Rate (l mole^{-1} sec^{-1})		
	k_H	k_D	k_H/k_D
DABCO	3.54×10^{-1}	3.62×10^{-1}	1.0
Et_3N	2.97×10^{-2}	2.63×10^{-2}	1.1
i-Pr_2EtN	4.90×10^{-3}	3.77×10^{-3}	1.3

The deuterium isotope effects are negligible, and may in fact be secondary isotope effects. The lack of a significant deuterium isotope effect amounts to confirmation that the energy diagram in Figure VIa correctly describes the reaction. It indicates that in the transition state the bond of the hydrogen to the base is essentially complete. This would be consistent with all three mechanisms proposed in the latter part of section B, if it is assumed that removal of the H is virtually complete in the transition state.

D. The Effect of Traps on the Rate of Reaction

The reaction of alkanesulfonyl chlorides with tertiary amines is second-order when no sulfene traps are present in the reaction mixture, or when trap concentration is low (5). When fairly substantial concentrations of certain traps were used, however, it was found that the rate of reaction increased, in some cases more than two-fold. This effect was observed when water, aniline, and *N*-methylaniline were used as traps in the reaction of methanesulfonyl chloride with triethylamine (5). Other examples were also reported (15). The rate expression that was found to fit the experimental results was

$$\text{Rate} = k_2[S][B] + k_3[S][B]\ [\text{trap}]$$

where S indicates sulfonyl chloride and B the tertiary amine.

It is known that the reaction described by the second-order term leads to the formation of sulfenes, as demonstrated by the appearance of monodeuterated products when deuterated traps are used (2). The mechanism described by the third-order term is not known. However, an experiment was done by Lee to demonstrate that it leads to a sulfene as well (15). A sulfene was generated by the action of triethylamine on methanesulfonyl chloride in the presence of a concentration of aniline-d_2 ($C_6H_5ND_2$) so that about 1/3 of the product would arise through the third-order term mechanism. The product was found to be almost exclusively monodeuterated, thus demonstrating that all of the reaction went through a sulfene.

The explanation for this acceleration of the rate by the trap has not been elucidated, and the following experiments were carried out to attempt to shed further light on this reaction.

Results and Discussion

A series of kinetic experiments were done, using methanesulfonyl chloride, tributylamine, and a number of substituted anilines. The procedure was as already described in sections B and C of Part IV. The temperature of all runs was 20°C, and dimethoxyethane was used as solvent.

Excellent pseudo-first-order plots were obtained for all runs. These experiments are listed in Table XIV, together with k_{obs} and $k_{obs}/[Bu_3N]$.

When the quantity $k_{obs}/[Bu_3N]$ was plotted against the trap concentration, a graph as in Figure VII was obtained. The value for zero concentration was the same in the plot for each aniline derivative. Figure VII, the plot for *p*-anisidine, is a rather good straight line; some of the other plots were less well correlated.

The equation for each line is

$$\frac{k_{obs}}{[Bu_3N]} = k_3[\text{trap}] + k_2$$

where [trap] signifies the concentration of the particular trap under consideration. For each amine, k_2 and k_3 (the

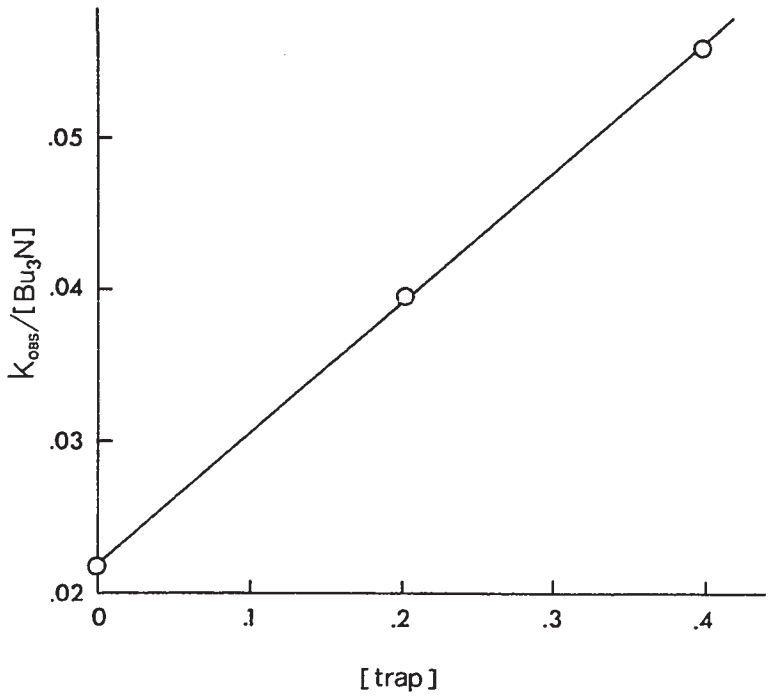

Fig. VII. Plot of $k_{obs}/[Bu_3N]$ against concentration of trap (*p*-anisidine).

TABLE XIV

Determination of the rate constants of the reaction of methanesulfonyl chloride with tributylamine in dimethoxyethane at 20.0°C in presence of substituted anilines as traps. Concentration of tributylamine was .04*M*.

Trap	[Trap] (moles l^{-1})	k_{obs} (sec^{-1})	$k_{obs}/[Bu_3N]$ ($l\ mole^{-1}\ sec^{-1}$)
None	-	0.845×10^{-3}	2.11×10^{-2}
p-NMe_2	0.200	2.74×10^{-3}	6.80×10^{-2}
p-NH_2	0.100	2.98×10^{-3}	7.45×10^{-2}
	0.200	5.13×10^{-3}	12.8×10^{-2}
p-OCH_3	0.204	1.55×10^{-3}	3.96×10^{-2}
	0.400	2.24×10^{-3}	5.60×10^{-2}
p-CH_3	0.199	1.31×10^{-3}	3.27×10^{-2}
	0.399	1.71×10^{-3}	4.27×10^{-2}
H	0.200	1.25×10^{-3}	3.12×10^{-2}
	0.401	1.58×10^{-3}	3.94×10^{-2}
m-OCH_3	0.200	1.41×10^{-3}	3.52×10^{-2}
	0.400	1.76×10^{-3}	4.39×10^{-2}

Continued on next page

TABLE XIV (cont'd)

Trap	[Trap] (moles l^{-1})	k_{obs} (sec^{-1})	$k_{obs}/[Bu_3N]$ ($l\ mole^{-1}\ sec^{-1}$)
p-Cl	0.0786	1.08×10^{-3}	2.69×10^{-2}
	0.200	1.43×10^{-3}	3.58×10^{-2}
	0.201	1.26×10^{-3}	3.14×10^{-2}
	0.310	1.44×10^{-3}	3.60×10^{-2}
	0.401	1.73×10^{-3}	4.31×10^{-2}
	0.408	1.72×10^{-3}	4.30×10^{-2}
m-Cl	0.199	1.17×10^{-3}	2.94×10^{-2}
	0.400	1.53×10^{-3}	3.83×10^{-2}
m-NO_2	0.100	1.11×10^{-3}	2.77×10^{-2}
	0.200	1.57×10^{-3}	3.91×10^{-2}
	0.200	1.59×10^{-3}	3.99×10^{-2}
	0.301	1.63×10^{-3}	4.06×10^{-2}
	0.404	1.80×10^{-3}	4.50×10^{-2}
p-NO_2	0.195	1.64×10^{-3}	4.22×10^{-2}
	0.400	2.60×10^{-3}	6.50×10^{-2}

intercept and slope of the graph, respectively) were obtained by least squares analyses. The values derived are tabulated in Table XV.

A Hammett plot may be constructed by plotting log k_3/k_0 against σ values (23), where k_0 is the value of k_3 for aniline. The plot is shown in Figure VIII. The shape of the line is not straight, but dished upward on the sides. It appears that both relatively basic and relatively acidic anilines are capable of efficiently carrying out the "third-order" mechanism.

One interpretation of the curved plot is that two independent mechanisms are operating, one with a positive ρ, the other with a negative ρ. In Figure VIII, the curve that was drawn through the points was calculated by assuming an additive effect of two processes, one with $\rho = 1.00$, the other with $\rho = -1.00$. The positive ρ mechanism may be one in which the aniline is hydrogen-bonded to a negatively charged moiety (*e.g.* Cl^-) in the transition state. Similarly the negative ρ may correspond to an interaction with a δ^+ in the transition state (*e.g.* $R_3\overset{+}{N}H$).

A contribution towards the third-order term may be due to hydrogen bonding of the tributylamine with the aniline derivative, with the formation of a hydrogen-bonded 1 : 1 complex. The aniline nitrogen in such a complex may be considerably more basic than the aniline by itself, and it may be capable of generating sulfene at a competitive rate.

TABLE XV

Determination of values of second-order (k_2) and third-order (k_3) rate constants for the reaction of methanesulfonyl chloride with tributylamine in the presence of substituted aniline traps, as given in previous table. Calculated from Rate vs. [Trap] graph.

Trap	Intercept=k_2 ($l\ mole^{-1}\ sec^{-1}$)	Slope=k_3 ($l\ mole^{-2}\ sec^{-1}$)	k_3/k_0	Log k_3/k_0
p-NMe_2	2.11×10^{-2}	23.5×10^{-2}	5.14	.711
p-NH_2	2.09×10^{-2}	26.7×10^{-2}	5.86	.768
p-OCH_3	2.13×10^{-2}	8.73×10^{-2}	1.91	.281
p-CH_3	2.14×10^{-2}	5.41×10^{-2}	1.19	.076
H	2.14×10^{-2}	4.56×10^{-2}	1.00	.000
m-OCH_3	2.20×10^{-2}	5.70×10^{-2}	1.25	.097
p-Cl	2.22×10^{-2}	5.09×10^{-2}	1.12	.049
m-Cl	2.10×10^{-2}	4.30×10^{-2}	0.943	-.026
m-NO_2	2.35×10^{-2}	6.00×10^{-2}	1.32	.121
p-NO_2	2.09×10^{-2}	10.98×10^{-2}	2.41	.382

Average value for $k_2 = 2.16 \times 10^{-2}$

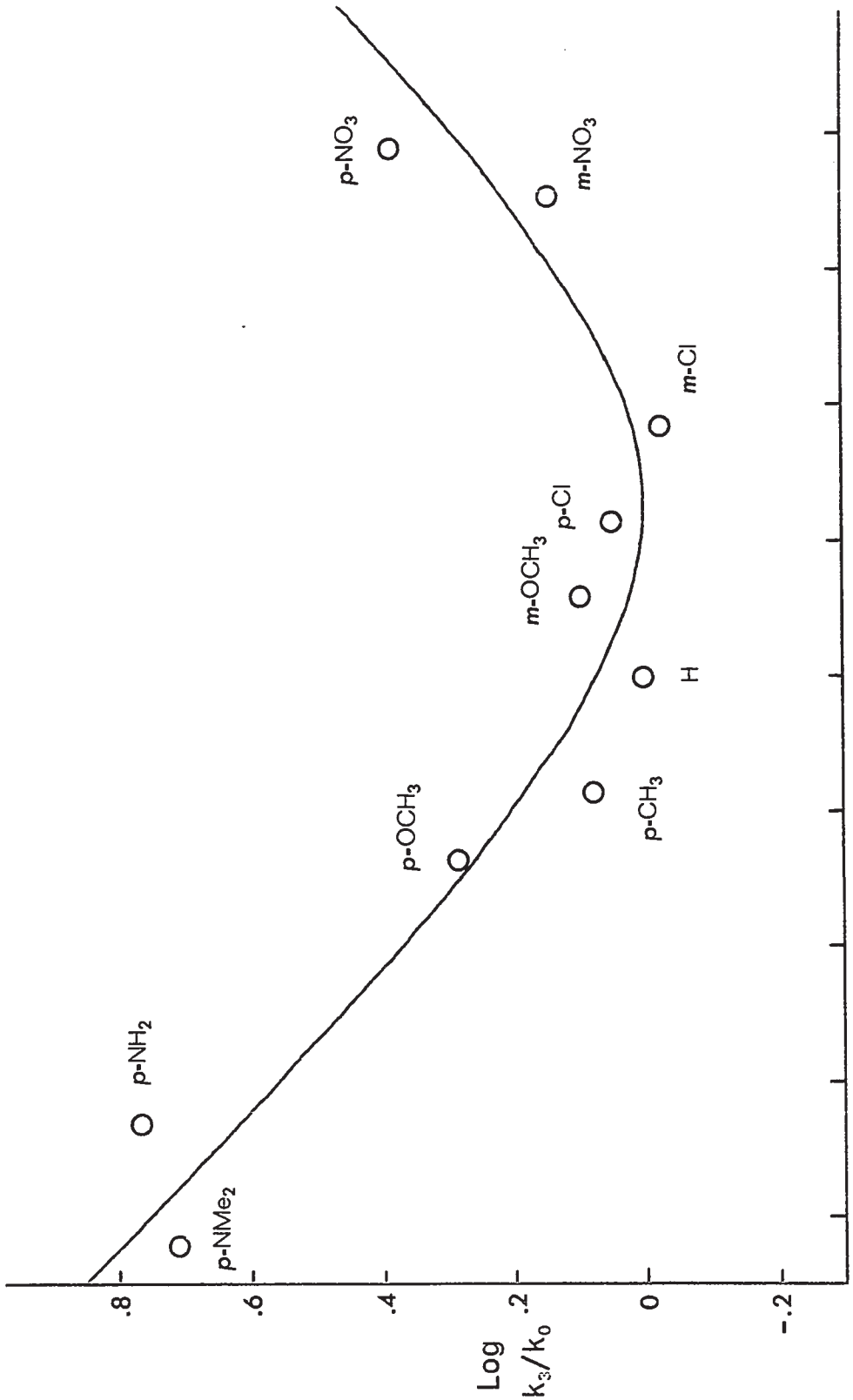

Fig. VIII. Hammett plot, showing log of the relative third-order rate constants plotted against σ.

However, it seems unlikely that this scheme by itself can account for the rather substantial magnitude of k_3 (it is larger than k_2 - in some cases by more than a factor of 10; this comparison of second- and third-order rate constants is valid if a bimolecular mechanism is assumed). For every mole of complex formed, a mole of tributylamine is lost. Therefore the complex must be considerably more basic than the tributylamine in order to account for the third-order rate constant. This seems unlikely; and if it is true, the equilibrium must be so much in favor of the free tributylamine and aniline, that only very small quantities of the hydrogen-bonded complex could be formed.

Experiments were also done with isopropyl alcohol as a trap. Previously, using Et_3N, no third-order term had been found for isopropyl alcohol (5). But with tributylamine a definite rate increase was noted, with k_3 found to be 1.04 x 10^{-2} 1 $mole^{-2}$ sec^{-1}. The relevant information may be found in Table XVI.

TABLE XVI

[*i*-PrOH]	k_{obs} (sec^{-1})	$k_{obs}/[Bu_3N]$ (1 $mole^{-1}$ sec^{-1})	k_3 (1 $mole^{-2}$ sec^{-1})
4.00×10^{-1}	1.01×10^{-3}	2.53×10^{-2}	1.04×10^{-2}
8.25×10^{-1}	1.19×10^{-3}	2.97×10^{-2}	

EXPERIMENTAL

Infra-red spectra were recorded on a Beckman IR-10 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer using 1.0 cm quartz cells. Nuclear magnetic resonance (n.m.r.) spectra were obtained on Varian A-60, T-60, and HA-100 instruments; signals are expressed in parts per million (p.p.m.) downfield from tetramethylsilane as internal standard (δ scale). Mass spectra were obtained on a Varian M-66 instrument. Refractive indices were determined with a thermostatically controlled Bausch and Lomb refractometer. Melting points were determined on a Kofler hot stage, and are uncorrected.

Methylene chloride and 1,2-dimethoxyethane were distilled from calcium chloride and calcium hydride, respectively. Methanesulfonyl chloride was distilled before use, and phenylmethanesulfonyl chloride was recrystallized from carbon tetrachloride. Triethylamine and pyridine were distilled after refluxing over calcium hydride, and tributylamine was distilled from potassium hydroxide pellets. Quinuclidine and 1,4-diazabicyclo[2,2,2]octane were sublimed. Deuterium oxide (99.8% D_2O) was supplied by Stohler Isotope Chemicals,

Montreal.

Microanalyses were performed by A. B. Gygli, Toronto. Deuterium analyses by the combustion method were carried out by J. Nemeth, Urbana, Ill.

I. COMPETITION EXPERIMENTS

A. The Competition of Chloride and Fluoride Ions

The phenylmethane-d_2-sulfonyl chloride used in these experiments was prepared by successive base-catalysed hydrolyses of natural abundance phenylmethanesulfonyl chloride with deuterium oxide, and treating the resulting sulfonate with phosphorus pentachloride. The method has been described by Durst (20). After five treatments the product was obtained in 57% overall yield, m.p. 92-93° after recrystallization from chloroform. Mass spectrum: weak peaks due to the parent ion were observed at *m/e* 191, 192, 193, and 194. Relative peak intensities were 5.8, 100, 8.9, and 36.8, respectively. The peak at 192, corresponding to $C_6H_5CD_2SO_2Cl$, contains a small CHD M+1 peak (about 0.51). Thus the corrected peak intensity at 192 is 99.5, and from these values the proportions of nondeuterated, monodeuterated, and dideuterated sulfonyl chlorides were calculated to be 0, 5.5, and 94.5 mole %, respectively.

Anal. A deuterium analysis was done by J. Nemeth. Calcd. for $C_7H_5D_2SO_2Cl$: 28.57 atom % excess deuterium. Found: 26.80 atom % excess deuterium.

1. Reaction of Phenylmethane-d_2-sulfonyl Chloride with Triethylamine and Fluoride Ion

A solution of triethylammonium fluoride and triethylamine was prepared as follows: anhydrous hydrogen fluoride gas (260 mg, 13.0 mmole) was condensed in a polyethylene bottle packed in crushed ice. The hydrogen fluoride was then dissolved in methylene chloride (60 ml) which had been cooled in ice. Triethylamine (3.80 ml, 2.76 g, 27.3 mmole) was added to the solution dropwise and with swirling.

The solution prepared above, containing approximately equimolar amounts of free triethylamine base and triethylammonium fluoride, was added with swirling to a solution of phenylmethane-d_2-sulfonyl chloride (143 mg, 0.751 mmole) in methylene chloride (20 ml). After 10 sec, excess base was destroyed by quickly adding concentrated hydrochloric acid (5.2 ml) to the reaction mixture. This procedure prevents extensive base-catalysed exchange of the sulfonyl fluoride hydrogens.

The reaction mixture was evaporated, ether was added, and an extraction with water carried out. The ether layer was dried ($MgSO_4$) was evaporated, and produced phenylmethane-*d*-sulfonyl fluoride (106 mg, 81% yield). It was recrystallized from carbon tetrachloride, m.p. 92.5-93.5°, lit. (40) 90-91°. Infra-red spectrum ($CHCl_3$): included peaks at 1495, 1452, 1403, and 1171 cm^{-1}.

N.m.r. spectrum ($CDCl_3$): δ 4.57 (approx. 1 H, multiplet), 7.46 (5 H, singlet). The methylene group at 4.57 consisted of a doublet of 1:1:1 triplets, resulting from coupling of the hydrogen with the fluorine and the geminal deuterium; J_{HF} = 3.3, J_{HD} = 2.2 Hz. In addition, a very small absorption (estimated as less than 10% of the methylene absorption) due to some non-deuterated sulfonyl fluoride could be detected as a doublet centred at 4.58 p.p.m., J = 3.1.

Mass spectrum: the parent ion was observed as a series of peaks at *m/e* 174-177, and their intensities were observed. These were 4.92, 100, 31.7, and 6.93 for *m/e* 174, 175, 176, and 177, respectively. From these values the proportions of the nondeuterated, monodeuterated, and di-deuterated sulfonyl fluorides were calculated to be 3.9, 78, and 18 mole %, respectively. This corresponds to an average deuterium content of 1.14 D in the methylene group.

The above figures were confirmed by a deuterium analysis: Found, 16.55 atom % excess D. This corresponds to a deuterium content of 1.16 D in the methylene group.

2. Competition Experiment: Fluoride and Chloride

A solution containing equimolar quantities of fluoride and chloride ions, and triethylamine, was prepared as follows: anhydrous hydrogen fluoride gas (129 mg, 6.45 mmole) was

condensed in a cooled polyethylene bottle as described before, cold methylene chloride (3 ml) was added, followed by triethylamine (1.90 ml, 13.7 mmole). This solution was added to one containing triethylammonium chloride (865 mg, 6.29 mmole) and the solution made up to 30 ml with methylene chloride.

The solution thus prepared was added with swirling to a solution of phenylmethane-d_2-sulfonyl chloride (76.2 mg, 0.396 mmole) in methylene chloride (10 ml). After 10 sec of reaction, excess base was destroyed by quickly adding concentrated hydrochloric acid (2.6 ml) to the reaction mixture. A workup was carried out as described in the previous experiment. A white product (60.8 mg, 88%) was obtained, m.p. 92.5-93.5° after recrystallization from carbon tetrachloride.

The n.m.r. spectrum was similar to that of the sulfonyl fluoride obtained in the previous experiment: δ 4.57 (approx. 1 H, multiplet), 7.45 (5 H, singlet). However, the product of this experiment showed considerably more of the doublet (approximately 20% in area) in the methylene region due to the non-deuterated sulfonyl fluoride. This suggests a 1:10 molar ratio for CH_2 : CHD.

Mass spectrum: the parent ion peaks were found to have intensities of 10.7, 100, 21.0, and 6.65 for *m/e* 174, 175, 176, and 177, respectively. From these values, the proportions of the nondeuterated, monodeuterated, and

dideuterated sulfonyl fluorides were calculated to be 8.8, 81, and 9.7 mole %, respectively. This corresponds to an average deuterium content of 1.01 D in the methylene group. The above figures were confirmed by a combustion deuterium analysis: Found, 14.70% excess D. This corresponds to a deuterium content of 1.03 D in the methylene group.

3. *Reaction of Phenylmethane-d_2-sulfonyl Chloride with Pyridine and Fluoride Ion*

This experiment was carried out in about the same way as the triethylamine and fluoride ion experiment. A solution containing anhydrous hydrogen fluoride (120 mg, 6.0 mmole) and pyridine (1.13 ml, 1.11 g, 14.1 mmole) in methylene chloride (30 ml) was added to a solution of phenylmethane-d_2-sulfonyl chloride (74.6 mg, 0.387 mmole) in methylene chloride (10 ml). The reaction mixture was allowed to stand at room temperature for 105 min, and concentrated hydrochloric acid (2.8 ml) was added. The workup was as already described, and the sulfonyl fluoride (65.4 mg, 96% yield) was obtained, m.p. 93-94°, mixed m.p. with authentic nondeuterated sulfonyl fluoride, 93-94°. Infra-red spectrum ($CHCl_3$): included peaks at 1495, 1454, 1406, and 1262 cm^{-1}. There was no evidence of any starting material. N.m.r. spectrum ($CHCl_3$): δ 4.50 (0.2 H, multiplet), 7.42 (5 H, singlet). The multiplet appeared to be a doublet of 1:1:1

triplets; there was no evidence for any doublet due to nondeuterated sulfonyl fluoride. It appears, therefore, that the product consists of 20% monodeuterated and 80% dideuterated material.

In a separate experiment, tetraethylammonium fluoride was reacted with phenylmethanesulfonyl chloride in chloroform. No amine was used. The reaction appeared to be complete in a few minutes, and the product (80% yield) proved to be phenylmethanesulfonyl fluoride, as shown by its n.m.r. spectrum and the m.p. (94-94.5° after a recrystallization from carbon tetrachloride).

B. Competition Experiments with Benzyl Mercaptan and Isopropyl Alcohol

1. Competition Reaction: Benzyl Mercaptan and Isopropyl Alcohol

A solution was prepared containing equimolar amounts of benzyl mercaptan (2.500 g, 20.15 mmole) and isopropyl alcohol (1.205 g, 20.05 mmole), together with pyridine (3.0 ml, 2.95 g, 37.3 mmole), in methylene chloride (20.0 ml). It was added quickly, and with swirling, to a solution of phenylmethanesulfonyl chloride (384 mg, 2.02 mmole) in methylene chloride (10.0 ml). The reaction was allowed to stand at room temperature for 25 min, after which the products

were isolated by evaporating the solvent, adding ether, and carrying out an efficient extraction with water. This aqueous layer, which was slightly basic, was saved.

The ether layer was washed successively with 10% hydrochloric acid, 10% sodium hydroxide, and water. After drying ($MgSO_4$) and evaporating, it was found to contain isopropyl phenylmethanesulfonate (507 mg, 84 mole %). The identity was proved by i.r. and n.m.r. spectroscopy.

The benzyl phenylmethanethiolsulfonate that might be expected to be formed is not stable under the reaction conditions, but decomposes to phenylmethanesulfinic acid (see later). Thus the aqueous layer that had been saved was acidified (HCl) and treated with chlorine gas to convert the sulfinic acid to sulfonyl chloride. A precipitate immediately appeared. An extraction with ether produced pure phenylmethanesulfonyl chloride (28.1 mg, 7.3 mole %), m.p. 89-91°, n.m.r. spectrum identical with authentic sulfonyl chloride.

The amount of sulfonyl chloride produced corresponds to the amount of benzyl mercaptan trapped by sulfene (except for losses). Therefore the trapping rate ratio was calculated to be 0.087 : 1 for benzyl mercaptan : isopropyl alcohol.

Since the total yield was approximately 91 mole % and since there is a possibility that less than 100% of the thiolsulfonate was converted to sulfonyl chloride (see below), we may express the amount of thiolsulfonate formed as 7.3 to 15 mole %. On this basis, the trapping rate ratio may be as high as 0.18 : 1.

2. Preparation of Benzyl Phenylmethanethiolsulfonate

A solution was prepared containing phenylmethanesulfonyl chloride (383 mg, 2.01 mmole) and benzyl mercaptan (250 mmole, 2.02 mmole) in methylene chloride. (A solution of these compounds was found to be stable for at least 7 days.) To this solution was added triethylamine (1.0 ml, 0.73 g, 7.2 mmole) with swirling.

After standing at room temperature for 10 min, the solvent was evaporated, ether added, and an extraction with water carried out. The ether layer was dried ($MgSO_4$) and evaporated and produced an oil (493 mg) which its n.m.r. spectrum revealed to be 63% benzyl phenylmethanethiolsulfonate (310 mg, 1.11 mmole) and 37% dibenzyl disulfide. Thus the crude yield is 55%. The product could be purified by recrystallization from chloroform (259 mg, 46% overall yield), m.p. 109.5-110.5°, lit. (41) 108°. Infra-red spectrum ($CHCl_3$): included peaks at 1496 (s), 1456 (s), 1329 (vs), 1142 (s), 1120 (vs), 1077 (m), 878 (m), and 699 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.07 (2 H, singlet), 4.25 (2 H, singlet), 7.37 (10 H, multiplet).

3. Reaction of Phenylmethanesulfonyl Chloride with Pyridine and Excess Benzyl Mercaptan

A solution containing benzyl mercaptan (2.487 g,

20.0 mmole) and pyridine (3.0 ml, 37.3 mmole) in methylene chloride (20.0 ml) was added with swirling to a solution of phenylmethanesulfonyl chloride (379 mg, 1.99 mmole) in methylene chloride (10 ml). After standing at room temperature for 25 min, the solvent was evaporated, ether added, and an extraction with water carried out. The aqueous layer was separated and acidified (HCl). It was treated with chlorine gas to convert any phenylmethanesulfinic acid to the sulfonyl chloride. Immediately a precipitate appeared. An extraction with ether produced phenylmethanesulfonyl chloride (168 mg, 44%), m.p. 91-92° after recrystallization from carbon tetrachloride.

In a similar experiment using phenylmethane-d_2-sulfonyl chloride it was shown that the sulfonyl chloride product contained one and only one hydrogen. N.m.r. spectrum ($CDCl_3$): δ 4.84 (1.0 H, 1:1:1 triplet), 7.45 (5 H, singlet). The methylene region at 4.84 showed no evidence of any di-deuterated material.

4. Experiments with Benzyl Phenylmethanethiolsulfonate

A solution of benzyl phenylmethanethiolsulfonate (44.9 mg), isopropyl alcohol (200 mg), and pyridine (500 mg) in methylene chloride (5.0 ml) was prepared. It was allowed to stand at room temperature for 70 min. After this time

the solvent was evaporated, ether added, and an extraction with water carried out. The ether layer was found to contain 44.0 mg of pure starting material (98% recovery) as identified by its n.m.r. spectrum. There was no evidence for any isopropyl phenylmethanesulfonate, or any other product.

In another experiment, the thiolsulfonate (50 mg) was dissolved in chloroform-*d* and placed in an n.m.r. tube. The spectrum was recorded at intervals. Little change was found in the spectrum after 14 h.

A control experiment was done on the thiolsulfonate to demonstrate that it decomposes to the sulfinic acid under reaction conditions of the competition experiment. A solution containing benzyl mercaptan (124 mg, 1.00 mmole), isopropyl alcohol (64.1 mg, 1.07 mmole) and pyridine (148 mg, 1.86 mmole) in methylene chloride (1.00 ml) was added to a solution of benzyl phenylmethanethiolsulfonate (24.7 mg, .089 mmole) in methylene chloride (0.50 ml). The reaction mixture was allowed to stand at room temperature for 25 min. The solvent was then evaporated, ether added, and an extraction with water carried out. The water layer was acidified (HCl) and chlorine gas bubbled in. A white precipitate appeared. An ether extraction produced pure phenylmethanesulfonyl chloride (18.0 mg, 100%), as identified by its n.m.r.

spectrum.

The original ether layer was washed with 10% sodium hydroxide, dried, and evaporated. It contained dibenzyl disulfide (210 mg, 100% based on thiolsulfonate), according to the n.m.r. spectrum. There was no evidence for any isopropyl phenylmethanesulfonate.

C. Competition Reactions Involving Phenylmethanesulfonyl Chloride and Aniline Derivatives

1. p-*Toluidine and* p-*Anisidine*

A solution was prepared containing equimolar quantities of *p*-anisidine (2.460 g, 19.97 mmole) and *p*-toluidine (2.138 g, 19.96 mmole), together with triethylamine (4.00 ml, 2.90 g, 28.7 mmole) in methylene chloride (20.0 ml). It was added quickly, and with swirling, to a solution of phenylmethanesulfonyl chloride (372 mg, 1.95 mmole) dissolved in methylene chloride (10.0 ml). The reaction mixture was allowed to stand at room temperature for 2 min. The mixture of sulfonamides was isolated by evaporating the methylene chloride, adding ether, and carrying out an efficient extraction with 5% hydrochloric acid. The ether layer, after drying ($MgSO_4$) and evaporating, yielded 501 mg of a viscous oil (95% yield, based on the sum of the sulfonamide product yields in mmoles).

The composition of the product was determined by nuclear magnetic resonance spectroscopy ($CDCl_3$), and the composition was calculated by considering the areas of the methyl peaks and the methylene region. The product was found to contain 46 mole % phenylmethanesulfon-*p*-toluidide and 54 mole % phenylmethanesulfon-*p*-anisidide. Accuracy of the method was estimated to be ± 3%. Confirmation of the analysis was obtained by preparing a known sample of composition close to that of the product, and demonstrating that the infra-red and n.m.r. spectra of the two samples superimposed. Thus the ratio of trapping rates was calculated as 1 : 1.17 (*p*-toluidine : *p*-anisidine).

The above experiment was repeated using the same quantities, except that only 0.5 ml of triethylamine was used. The product contained 44 mole % phenylmethanesulfon-*p*-toluidide and 56 mole % phenylmethanesulfon-*p*-anisidide, and the trapping ratio ratio was calculated as 1 : 1.27 (*p*-toluidine : *p*-anisidine).

2. p-*Toluidine and Aniline*

The traps, *p*-toluidine (1.602 g, 14.95 mmole) and aniline (1.403 g, 15.07 mmole), were dissolved with triethylamine as described above, except that the reaction was carried out on a 2/3 scale. After the reaction had been worked up,

398 mg (100%) of product was isolated. It was found to be 62 mole % phenylmethanesulfon-*p*-toluidide and 38 mole % phenylmethanesulfonanilide. The trapping rate ratio was calculated to be 1 : 0.61 (*p*-toluidine : aniline).

3. p-*Toluidine and* m-*Anisidine*

The procedure described above was repeated with *p*-toluidine (2.139 g, 19.96 mmole) and *m*-anisidine (2.474 g, 20.09 mmole). The product (523 mg, 96%) was found to contain 66 mole % phenylmethanesulfon-*p*-toluidide and 34 mole % phenylmethanesulfon-*m*-anisidide. The trapping rate ratio was calculated to be 1 : 0.51 (*p*-toluidine : *m*-anisidine).

4. p-*Toluidine and* p-*Chloroaniline*

The procedure described above was repeated using *p*-toluidine (2.124 g, 19.86 mmole) and *p*-chloroaniline (2.572 g, 20.15 mmole). The product (525 mg, 100%) was found to be 73 mole % phenylmethanesulfon-*p*-toluidide and 23 mole % phenylmethanesulfon-*p*-chloroanilide. In addition a small amount of material (4 mole %), identified as bis(phenylmethanesulfon)-*p*-chloroanilide, was detected as a singlet at 4.74 p.p.m. This material was found to be insoluble in aqueous base, and was separated from the other components by washing an ether solution with a 5% potassium hydroxide solution. The ether

layer contained a white crystalline material (25 mg), m.p. 195.5 - 196.5° after recrystallization from acetonitrile. Infra-red spectrum ($CHCl_3$): included peaks at 1489 (s), 1378 (vs), 1357 (vs), 1160 (vs), 1141 (s), 1095 (m), and 907 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.85 (4 H, singlet), 6.1-7.1 (4 H, A_2B_2 multiplet), 7.44 (10 H, singlet). For purposes of calculating the trapping rate ratio, the bis compound was included mole for mole with the phenylmethanesulfon-*p*-chloroanilide.

The error in estimating the *p*-chloroanilide was approximately ± 10% in this experiment, since the methylene absorption overlaps with that of the more abundant *p*-toluidide. The methylene absorption due to the *p*-toluidide could be calculated from the absorption of the methyl group, and the absorption due to the *p*-chloroanilide was obtained by difference. The trapping rate ratio was calculated to be 1 : 0.37 (*p*-toluidine : *p*-chloroaniline).

5. p-*Toluidine and* m-*Chloroaniline*

In order to minimize formation of bis(phenylmethanesulfon)-*m*-chloroanilide, the amount of triethylamine in this experiment was reduced from 4.00 ml to 0.50 ml (3.59 mmole). Otherwise the experiment was carried out in the same way, using *p*-toluidine (2.160 g, 20.15 mmole) and *m*-chloroaniline (2.562 g, 20.08 mmole). The product (579 mg, 100%) was found

to be 81 mole % phenylmethanesulfon-*p*-toluidide, 17 mole % phenylmethanesulfon-*m*-chloroanilide, and 2.5 mole % bis-(phenylmethanesulfon)-*m*-chloroanilide. The bis compound was isolated by removing the other components by an alkaline extraction. The product (15 mg) was recrystallized from acetonitrile (m.p. 197-199°) and its i.r. and n.m.r. spectra were identical with those of the fully characterized compound. Accuracy of the *m*-chloroanilide determination was estimated to be ± 15% (see previous experiment). The trapping rate ratio was calculated as described before, and was found to be 1 : 0.24 (*p*-toluidine : *m*-chloroaniline).

6. p-*Toluidine and* m-*Nitroaniline*

This experiment was done with *p*-toluidine (2.154 g, 20.10 mmole) and *m*-nitroaniline (2.765 g, 20.01 mmole), and in order to minimize formation of bis(phenylmethanesulfon)-*m*-nitroanilide, only 0.50 ml of triethylamine was used. The product (535 mg, 100%) was found to be 89 mole % phenylmethanesulfon-*p*-toluidide, 9 mole % phenylmethanesulfon-*m*-nitroanilide, and 2 mole % bis(phenylmethanesulfon)-*m*-nitroanilide. The accuracy of the *m*-nitroanilide estimate is approximately ± 20%, for reasons already given. The trapping rate ratio was calculated to be 1 : 0.12 (*p* -toluidine : *m*-nitroaniline).

7. *Aniline and* m-*Anisidine*

The traps used were aniline (1.857 g, 19.94 mmole) and *m*-anisidine (2.475 g, 201.10 mmole), and the experiment was carried out as for the *p*-anisidine and *p*-toluidine experiment described earlier. The product (521 mg, 98%) was found to be 55 mole % phenylmethanesulfonanilide and 45 mole % phenylmethanesulfon-*m*-anisidide. The uncertainty was estimated to be ± 3%. The trapping rate ratio was calculated to be 1 : 0.82 (aniline : *m*-anisidine).

D. Various Competition Reactions Involving Sulfonyl Chlorides and Amines

1. *Methanesulfonyl Chloride, Triethylamine,* p-*Toluidine and Aniline*

The procedure is essentially the same as that with phenylmethanesulfonyl chloride (see section C). The two traps, *p*-toluidine (1.079 g, 10.07 mmole) and aniline (0.933 g, 10.02 mmole), were dissolved with triethylamine (2.00 ml, 1.45 g, 14.4 mmole) in methylene chloride (10.0 ml), and the solution was added rapidly to a solution of methanesulfonyl chloride (0.214 g, 1.87 mmole) in methylene chloride (5.0 ml). The reaction mixture was allowed to stand at room temperature for 1.0 h, and then worked up in the usual way. The

product (328 mg, 97% yield, based on the sum of the product yields in mmoles) contained 67 mole % methanesulfon-*p*-toluidide and 33 mole % methanesulfonanilide. The trapping rate ratio was calculated to be 1 : 0.49 (*p*-toluidine : aniline).

2. *Phenylmethanesulfonyl Chloride, Pyridine,* p-*Toluidine and Aniline*

The two traps, *p*-toluidine (2.140 g, 19.97 mmole) and aniline (1.871 g, 20.10 mmole) with pyridine as base (4.00 ml, 3.93 g, 49.7 mmole), were dissolved in methylene chloride (20.0 ml), and added quickly to a solution of phenylmethanesulfonyl chloride (0.384 g, 2.01 mmole) in methylene chloride (10.0 ml). After standing at room temperature for 40 min, the reaction mixture was worked up in the usual way. The product (498 mg, 96%) contained 71 mole % phenylmethanesulfon-*p*-toluidide and 29 mole % phenylmethanesulfonanilide. The trapping rate ratio was calculated to be 1 : 0.41 (*p*-toluidine : aniline).

3. *Phenylmethanesulfonyl Chloride, Triethylamine, Diethylamine and* p-*Toluidine*

The traps, diethylamine (1.464 g, 20.02 mmole) and *p*-toluidine (2.145 g, 20.01 mmole) were dissolved in methylene

chloride (20.0 ml) with triethylamine (4.00 ml, 2.90 g, 28.7 mmole). This solution was added quickly to a solution of phenylmethanesulfonyl chloride (0.385 g, 2.02 mmole) dissolved in methylene chloride (10.0 ml).

After standing at room temperature for 1.0 min, the mixture was worked up by evaporating the methylene chloride, adding ether, and carrying out an efficient extraction with 5% hydrochloric acid. The ether layer was then thoroughly washed with 5% sodium hydroxide solution, dried ($MgSO_4$), and evaporated. The crystalline product (324 mg, 71 mole %) was identified by its i.r. and n.m.r. spectra as pure *N,N*-diethylphenylmethanesulfonamide. The sodium hydroxide solution was acidified (conc. hydrochloric acid) and extracted with ether. The ether layer, after drying ($MgSO_4$) and evaporating, yielded a white crystalline solid (126 mg, 24 mole %), m.p. 112-113° after recrystallization from benzene, and was identified as pure phenylmethanesulfon-*p*-toluidide. The trapping rate ratio was calculated to be 1 : 3.0 (*p*-toluidine : diethylamine.

4. *Phenylmethanesulfonyl Chloride, Diethylamine and* p-*Toluidine*

A solution of diethylamine (1.475 g, 20.16 mmole) and *p*-toluidine (2.130 g, 19.88 mmole) in methylene chloride (20.0 ml) was prepared. No other base was added, the

diethylamine serving as the dehydrohalogenating base in this experiment. The solution was added quickly to a solution of phenylmethanesulfonyl chloride (385 mg, 2.02 mmole) in methylene chloride (10.0 ml).

The reaction mixture was allowed to stand at room temperature for 1.0 min, after which a workup similar to the previous experiment was carried out. The products were pure crystalline *N,N*-diethylphenylmethanesulfonamide (417 mg, 91 mole %), and pure crystalline phenylmethanesulfon-*p*-toluidide (33 mg, 6.2 mole %), m.p. 113-114° after recrystallization from benzene. The trapping rate ratio was calculated to be 1 : 15 (*p*-toluidine : diethylamine).

E. Competition Reactions Involving Alcohols and Phenols

1. Methanesulfonyl Chloride, Triethylamine, Phenol and p-*Toluidine*

The procedure was similar to the competition experiments already described. A solution was prepared containing phenol (0.943 g, 10.02 mmole), *p*-toluidine (1.071 g, 10.00 mmole), and triethylamine (2.0 ml, 1.45 g, 14.4 mmole) in methylene chloride (10 ml), and it was added with swirling to a solution of methanesulfonyl chloride (227 mg, 1.99 mmole) in methylene chloride (10 ml). The reaction mixture was allowed to stand at room temperature for 10 min, after which

the solvent was evaporated, ether added, and an extraction carried out with 10% hydrochloric acid. The acidic extraction was followed by an extraction with 10% sodium hydroxide. The ether layer was separated, dried ($MgSO_4$), and evaporated to produce a white solid (279 mg, 82 mole %) which was shown to be pure phenyl methanesulfonate by its n.m.r. spectrum. A recrystallization from carbon tetrachloride gave a white crystalline material, m.p. 60-61°.

The sodium hydroxide layer was acidified (HCl) and extracted with ether. A product was obtained containing phenol and methanesulfon-*p*-toluidide. It was found that the phenol could be removed by sublimation, and the product was found to contain the *p*-toluidide (44.5 mg, 15 mole %) as indicated by its n.m.r. spectrum.

The trapping rate ratio was found to be 5.5 : 1 (phenol : *p*-toluidine).

2. *Phenylmethanesulfonyl Chloride, Triethylamine, Phenol and* p-*Toluidine*

This experiment was done as the previous experiment, using phenylmethanesulfonyl chloride (386 mg, 2.026 mmole) in methylene chloride (10 ml). The trap solution contained phenol (1.866 g, 19.84 mmole), *p*-toluidine (2.126 g, 19.86 mmole), and triethylamine (4.00 ml) in methylene chloride (20 ml). After carrying out the workup procedure already

described, pure phenyl methanesulfonate (390 mg, 78 mole %) was isolated. In addition, the methanesulfon-*p*-toluidide (91.1 mg, 17 mole %) was isolated. The trapping rate ratio was calculated to be 4.5 : 1 (phenol : *p*-toluidine).

3. Phenylmethanesulfonyl Chloride, Pyridine, Phenol, and p-*Toluidine*

The experiment was carried out as above, using phenol (1.877 g, 19.95 mmole), *p*-toluidine (2.142 g, 20.00 mmole), and pyridine (3.0 ml, 2.95 g, 37.3 mmole). The extractions produced phenyl phenylmethanesulfonate (175 mg, 35 mole %) and phenylmethanesulfon-*p*-toluidide (327 mg, 62 mole %). Hence the trapping rate ratio was calculated to be 0.56 : 1 (phenol : *p*-toluidine).

4. Phenylmethanesulfonyl Chloride, Triethylamine, Isopropyl Alcohol and p-*Toluidine*

The experiment was carried out as above, using isopropyl alcohol (1.204 g, 19.98 mmole), *p*-toluidine (2.142 g, 19.98 mmole), and triethylamine (4.0 ml). After the workup, which used an acid extraction but not a base extraction, a product was obtained (460 mg, 94% yield) which was indicated by n.m.r. and i.r. spectra to be isopropyl phenylmethanesulfonate (115 mg, 29 mole %) and phenylmethanesulfon-*p*-toluidide (345 mg, 71 mole %). The trapping rate ratio was calculated

to be 0.40 : 1 (isopropyl alcohol : *p*-toluidine).

5. *Phenylmethanesulfonyl Chloride, Pyridine, Isopropyl Alcohol and* p-*Toluidine*

The experiment was done as before, using isopropyl alcohol (1.200 g, 19.98 mmole), *p*-toluidine (2.139 g, 19.97 mmole), and pyridine (4.0 ml, 3.93 g, 49.6 mmole). As in the previous experiment, a base extraction was not done. The reaction product (439 mg, 92%) was found to be isopropyl phenylmethanesulfonate (198 mg, 50 mole %) and phenylmethanesulfon-*p*-toluidide (241 mg, 50 mole %). The trapping rate ratio is thus 1.0 : 1

F. Competition Experiment with Piperidine and Water

A solution containing piperidine (5.30 g, 62.2 mmole) and water (10.0 g, 555 mmole) in dimethoxyethane (75 ml) was mixed with swirling with a solution of methanesulfonyl chloride (3.450 g, 30.2 mmole) in dimethoxyethane (75 ml). The reaction was allowed to stand at room temperature for 10 min, after which the solvent was removed, ether added, and an extraction carried out with dilute hydrochloric acid. The ether layer was separated, dried ($MgSO_4$), and evaporated. The product (4.817 g, 98% crude yield) was identified by n.m.r. and i.r. spectra as pure methanesulfonpiperidide.

A recrystallization from chloroform (3.999 g, 81% overall) gave white plates, m.p. 48-49.5°C, lit. (42) 48-49°C. Infra-red spectrum (CCl_4): included peaks at 1446 (m), 1328 (vs), 1165 (s), 1151 (s), 1056 (m), 961 (s), and 936 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 1.63 (6 H, multiplet), 2.76 (3 H, singlet), 3.20 (4 H, multiplet).

No attempt was made to identify the sulfonic acid resulting from trapping of water. The trapping rate ratio cannot therefore be determined, but it is estimated from the high yield of crude piperidide that it is at least 450 : 1 in favour of piperidine.

II. PREPARATION OF COMPOUNDS

*1. Preparation of Phenylmethanesulfon-*p*-anisidide*

A solution was prepared containing *p*-toluidine (1.508 g, 12.2 mmole) and phenylmethanesulfonyl chloride (386 mg, 2.03 mmole) in methylene chloride (30 ml) and to it was added triethylamine (3.0 ml, 2.17 g, 21.5 mmole). The reaction mixture was allowed to stand at room temperature for 1.0 min, after which the solvent was evaporated, ether added, and an extraction carried out with 5% hydrochloric acid. The ether layer was separated, dried ($MgSO_4$), and evaporated, affording the product as an oil (558 mg, 99.3% crude yield) which crystallized on long standing. White

granular crystals were obtained from carbon tetrachloride (522 mg, 93% recrystallized yield), m.p. 90-91°, lit. (43) m.p. 103°. Infra-red spectrum ($CHCl_3$): included peaks at 1507 (s), 1391 (m), 1335 (s), 1250 (s), 1157 (vs), and 1036 cm^{-1} (s). Nuclear magnetic resonance (n.m.r.) spectrum ($CDCl_3$): δ 3.60 (3 H, singlet), 4.22 (2 H, singlet), 6.60 (1 H, broad singlet), 6.93 (4 H, A_2B_2 multiplet), 7.27 (5 H, singlet).

Anal. Calcd. for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.57. Found: C, 60.35; H, 6.02; N, 5.17; S, 11.60.

*2. Preparation of Phenylmethanesulfon-*p*-toluidide*

The preparation was as described for the *p*-anisidide, using *p*-toluidine (4.248 g, 39.6 mmole) and phenylmethanesulfonyl chloride (769 mg, 4.03 mmole) in methylene chloride (20.0 ml). The crude product was a solid (1.039 g, 98.6%) and was recrystallized from benzene (984 mg white crystals, 93%), m.p. 113-114°, lit. (44) 113°. Infra-red spectrum ($CHCl_3$): included peaks at 1509 (s), 1391 (s), 1336 (s), 1302 (m), 1156 (vs), and 1129 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 2.33 (3 H, singlet), 4.28 (2 H, singlet), 6.65 (1 H, broad singlet), 7.11 (4 H, singlet), 7.34 (5 H, singlet).

3. Preparation of Phenylmethanesulfonanilide

The preparation was as described for the *p*-anisidide, using aniline (3.736 g, 41.0 mmole) and phenylmethanesulfonyl chloride (752 mg, 3.94 mmole) in methylene chloride (20.0 ml). The crude product was a solid (918 mg, 94% crude yield) and was recrystallized from benzene (893 mg, 92% yield), m.p. 102-103°, lit. (44), 103.5°. Infra-red spectrum ($CHCl_3$): included peaks at 1597 (s), 1494 (s), 1405 (s), 1346 (s), 1154 (vs), and 1130 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.31 (2 H, singlet), 6.92 (1 H, broad singlet), 7.22, 7.29, and 7.32 (10 H, multiplet).

*4. Preparation of Phenylmethanesulfon-*m*-anisidide*

The preparation was as described for the *p*-anisidide, using *m*-anisidine (2.473 g, 20.1 mmole) and phenylmethanesulfonyl chloride (382 mg, 2.01 mmole) in methylene chloride (30 ml). The product was an oil (543 mg, 97.4% crude yield) which crystallized on long standing. It was recrystallized from chloroform (520 mg of white crystals, 92%), m.p. 80-81°. Infra-red spectrum ($CHCl_3$): included peaks at 1609 (vs), 1499 (s), 1393 (m), 1334 (s), 1281 (m), 1149 (vs), 1130 (s), 1050 (m), and 968 cm^{-1} (m). N.m.r. spectrum ($CDCl_3$): δ 3.78 (3 H, singlet), 4.32 (2 H, singlet), 6.64 (1 H, broad singlet), 6.76 (4 H, multiplet), 7.30 (5 H, singlet).

Anal. Calcd. for $C_{14}H_{15}NO_3S$: C, 60.63; H, 5.45; N, 5.05; S, 11.56. Found: C, 60.75; H, 5.70; N, 5.19; S, 11.55.

*5. Preparation of Phenylmethanesulfon-*p*-chloroanilide*

The preparation was as described for the *p*-anisidide, using *p*-chloroaniline (5.162 g, 40.5 mmole) and phenylmethanesulfonyl chloride (748.2 mg, 3.93 mmole) in methylene chloride (20 ml). The product was a white solid (1.040 g, 94% crude yield) and was recrystallized from chloroform (999 mg, 91%), m.p. 110.5-111.5°, lit. (43) 110°. Infrared spectrum ($CHCl_3$): 1491 (vs), 1390 (s), 1333 (vs), 1155 (vs), 1131 (s), and 1093 cm^{-1} (m). N.m.r. spectrum ($CDCl_3$): δ 4.27 (2 H, singlet), 6.86 (broad singlet), 7.10 (A_2B_2 multiplet), 7.25 (singlet). The low field absorption together integrated for 10 H.

Anal. Calcd. for $C_{13}H_{12}ClNO_2S$: C, 55.42; H, 4.29; Cl, 12.59; N, 4.97; S; 11.38. Found: C, 55.61; H, 4.43; Cl, 12.70; N, 4.83; S, 11.56.

*6. Preparation of Phenylmethanesulfon-*m*-chloroanilide*

The preparation was as described for the *p*-anisidide, using *m*-chloroaniline (2.318 g, 18.0 mmole) and phenylmethanesulfonyl chloride (389 mg, 2.04 mmole) in methylene chloride

(30 ml). The product was a white solid (439 mg), and on the basis of the n.m.r. spectrum was estimated to be 71% (1.11 mmole or 54% yield) phenylmethanesulfon-*m*-chloroanilide and 29% (0.29 mmole or 29% yield, based on phenylmethanesulfonyl chloride) of bis(phenylmethanesulfon)-*m*-chloroanilide.

The crude product was dissolved in ether and an extraction with 5% sodium hydroxide was carried out. The ether layer, after drying ($MgSO_4$) and evaporating, was found to contain 101 mg (23%) of the bis compound; it exhibited peaks at δ 4.80 (singlet), 6.07 and 6.23 (multiplets), 6.75-7.2 (multiplets), and 7.37 (singlet), in the n.m.r. spectrum ($CDCl_3$). This compound was fully characterized in a separate experiment.

The aqueous layer, upon acidification (HCl) and extraction (ether) afforded a white crystalline solid (337 mg, 58%), which was recrystallized from CCl_4 (312 mg, 54% overall yield), m.p. 105.5-106.5°, lit. (45) m.p. 102°. It was shown to be the *m*-chloroanilide by its infra-red spectrum ($CHCl_3$): 1592 (s), 1475 (s), 1390 (m), 1331 (s), 1156 (vs), and 1130 cm^{-1} (s); and its n.m.r. spectrum ($CDCl_3$): δ 4.27 (2 H, singlet), 7.07 (multiplet), 7.23 (singlet). The low field absorption integrated for 10 H.

Anal. Calcd. for $C_{13}H_{12}ClNO_2S$: C, 55.42; H, 4.29; Cl, 12.59; N, 4.97; S, 11.38. Found: C, 55.52; H, 4.20; Cl, 12.74; N, 5.08; S, 11.22.

7. Preparation of Phenylmethanesulfon-m-nitroanilide

A solution of *m*-nitroaniline (2.746 g, 19.9 mmole) and triethylamine (0.50 ml, 0.362 g, 3.6 mmole) methylene chloride (30 ml) was prepared. (The amount of triethylamine was reduced in this experiment to minimize formation of the nitroanilide anion and subsequent formation of bis(phenylmethanesulfon)-*m*-nitroanilide.) The solution was added to a solution of phenylmethanesulfonyl chloride (379 mg, 1.99 mmole) in methylene chloride (10 ml). The reaction mixture, after standing for 2.0 min at room temperature, was worked up as described for the *m*-chloroanilide. A solid material (204 mg, 41%) was obtained which appeared to be the bis compound. N.m.r. spectrum ($CDCl_3$): δ 4.85 (singlet), 7.39 (singlet), 6.3-8.0 (multiplets). This product was not further characterized.

The base-soluble material (243 mg, 42% crude yield) was recrystallized from chloroform (218 mg, 37% overall yield), m.p. 150-150.5°, lit. (45) 148°. Infra-red spectrum (Nujol mull): included peaks at 1528 (vs), 1490 (s), 1350 (vs), 1332 (vs), 1161 (vs), and 1127 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.32 (2 H, singlet), 6.99 (1 H, broad singlet), 7.2-8.0 (multiplet), 7.26 (singlet). The region 7.2-8.0 integrated for a total of 9 H.

Anal. Calcd. for $C_{13}H_{12}N_2O_4S$: C, 53.42; H, 4.14; N, 9.58; S, 10.97. Found: C, 53.20; H, 4.28; N, 9.77; S, 11.05.

8. Preparation of Bis(phenylmethanesulfon)-m-chloroanilide

A solution of phenylmethanesulfon-*m*-chloroanilide (242 mg, 0.858 mmole) and triethylamine (1.0 ml, 0.725 g, 7.17 mmole) in methylene chloride (7.5 ml) was added quickly to a solution of phenylmethanesulfonyl chloride (163 mg, 0.858 mmole) in methylene chloride (7.5 ml). The reaction mixture was allowed to stand at room temperature for 1.0 min, after which the solvent was evaporated and ether and acetonitrile were added. An extraction with 5% potassium hydroxide was carried out, and the organic layer, after drying ($MgSO_4$) and evaporating, produced a white solid (219 mg, 59%). The product was recrystallized from acetonitrile, and pure white crystals were obtained, m.p. 199-200°. Infra-red spectrum ($CHCl_3$): included peaks at 1584 (m), 1377 (vs), 1358 (s), 1160 (s), 1141 (m), and 934 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.85 (4 H, singlet), 6.10 and 6.25 (2 H, multiplets), 6.8-7.4 (2 H, multiplets), 7.43 (10 H, singlet).

Anal. Calcd. for $C_{20}H_{18}ClNO_4S_2$: C, 55.10; H, 4.16; Cl, 8.13; N, 3.21; S, 14.71. Found: C, 55.53; H, 4.93; Cl, 8.33; N, 3.33; S, 14.84.

A substantial amount of a white solid was noted upon acidification (HCl) of the basic aqueous layer. This material was assumed to be unreacted phenylmethanesulfon-*m*-chloroanilide.

9. Preparation of N,N-*Diethyl Phenylmethanesulfonamide*

A solution of diethylamine (2.0 ml, 1.42 g, 19.4 mmole) in methylene chloride (20 ml) was added to a solution of phenylmethanesulfonyl chloride (363 mg, 1.90 mmole) in methylene chloride (10 ml). The reaction mixture was allowed to stand at room temperature for 10 min, after which it was evaporated to dryness. Ether was added and an extraction with water carried out. The product was a low-melting solid (427 mg, 98.8%). The crude product was recrystallized in the cold (5°) from pentane-methylene chloride and a white product (146 mg, 34% overall) was obtained, m.p. 32.5-35°, lit. (46) 29°. Infra-red spectrum (CCl_4): included peaks at 1381 (m), 1334 (vs), 1202 (s), 1149 (s), 1124 (s), 1021 (s), and 940 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 1.07 (triplet, J = 7.0), 3.08 (quartet, J = 7.0), 4.17 (singlet), 7.31 (singlet).

10. Preparation of Phenyl Phenylmethanesulfonate

The preparation was as described in the previous experiment, using phenol (3.757 g, 40.0 mmole) and phenylmethanesulfonyl chloride (759 mg, 3.98 mmole) in methylene chloride (10 ml). Triethylamine (5.0 ml, 3.63 g, 35.9 mmole) was added, and the reaction mixture allowed to stand for 15 min. The extractions produced a white solid (959 mg, 97% crude yield), and was recrystallized from carbon tetrachloride (938

mg, 95% overall), m.p. 86-87°, lit. (47) 86.7-87.1°. Infra-red spectrum ($CHCl_3$): included peaks at 1486 (s), 1374 (vs), 1168 (s), 1145 (vs), and 869 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 4.51 (2 H, singlet), 7.0-7.4 (multiplet), 7.49 (singlet). The low-field absorption integrated for 10 H.

11. Preparation of Isopropyl Phenylmethanesulfonate

Triethylamine (5.0 ml, 3.63 g, 35.9 mmole) was added to a solution of isopropyl alcohol (2.402 g, 40.0 mmole) and phenylmethanesulfonyl chloride (753 mg, 3.95 mmole) in methylene chloride (20 ml). After standing at room temperature for 10 min, the solvent was evaporated and ether added. An extraction with water was carried out. The ether layer was separated, dried ($MgSO_4$), and evaporated. A low-melting solid (805 mg, 95% crude yield) was obtained. White crystals (786 mg, 93% overall) were obtained from recrystallization with carbon tetrachloride in the cold (5°). M.p. 46.5-47.5°, lit. (20) 46-47°. Infra-red spectrum ($CHCl_3$): included peaks at 1390 (m), 1358 (vs), 1346 (vs), 1171 (vs), 1138 (m), 1095 (m), 922 (vs), and 894 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 1.29 (2 H, doublet, J = 6.2), 4.33 (2 H, singlet), 4.79 (1 H, septet, J = 6.2), 7.44 (5 H, singlet).

12. Preparation of Methanesulfonanilide

The preparation was as given in the previous preparation, using aniline (1.866 g, 20.0 mmole) and methanesulfonyl chloride (225 mg, 1.96 mmole). The product (306 mg, 91%) was recrystallized from $CHCl_3$ to yield granular white crystals (280 mg, 83%), m.p. 99-100°, lit. (48) 98-99°. Infra-red spectrum ($CHCl_3$): included peaks at 1599 (s), 1493 (s), 1401 (s), 1335 (vs), 1153 (vs), and 973 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 3.03 (singlet), 7.32 (broad singlet).

13. Preparation of Methanesulfon-p-toluidide

A solution of *p*-toluidine (2.201 g, 20.5 mmole) and methanesulfonyl chloride (213 mg, 1.86 mmole) in methylene chloride (10 ml) was prepared, and to it was added triethylamine (2.0 ml, 1.45 g, 14.4 mmole). The reaction mixture was allowed to stand at room temperature for 1.0 h, after which the solvent was evaporated. Ether was added and an extraction carried out with 10% hydrochloric acid. The crude product contained 326 mg (94%) of methanesulfon-*p*-toluidide, and was recrystallized from chloroform to give white crystals (266 mg, 77%), m.p. 102.5-103.5°, lit. (49) 103-104°. Infra-red spectrum ($CHCl_3$): included peaks at 1510 (s), 1384 (m), 1330 (vs), 1300 (m), 1154 (vs), and 977 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 2.34 (3 H, singlet), 2.98 (3 H, singlet),

7.06 (1 H, broad singlet), 7.17 (4 H, singlet).

14. Preparation of N*-Butyl Methanesulfonamide*

Methanesulfonyl chloride (2.294 g, 20.0 mmole) and butylamine (3.05 g, 41.7 mmole) were dissolved in ether (50 ml). A precipitate resulted. After standing at room temperature for 10 min, an extraction with water was carried out. The ether layer was found to contain the amide as a white oil (2.670 g, 88%) which crystallized readily on cooling in ice. The product was distilled using a cold-finger apparatus (bath temperature 130-135°, 0.10 mm). Infra-red spectum (CCl_4): included peaks at 1320 (vs), 1150 (vs), 1081 (m), 976 (m), and 854 cm^{-1} (w), lit. (50) 1083, 978, 855 cm^{-1} . N.m.r. spectrum ($CDCl_3$): δ 0.8 to 1.8 (7 H, multiplets), 2.97 (3 H, singlet), 2.9 to 3.4 (2 H, multiplet), 5.0 (1 H, broad absorption). When a trace of quinuclidine was added, the multiplet at 2.9 to 3.4 p.p.m. resolved to a triplet at 3.14 p.p.m., J = 6.8 Hz.

15. Preparation of Phenyl Methanesulfonate

A solution containing phenol (1.831 g, 19.5 mmole) and methanesulfonyl chloride (221 mg, 1.93 mmole) in methylene chloride (10 ml) was prepared, and to it was added triethylamine (2.0 ml, 1.45 g, 14.4 mmole). The reaction mixture was allowed

to stand at room temperature for 1.0 h, after which the solvent was evaporated, ether added, and a 10% hydrochloric acid extraction carried out. This was followed by an extraction with 10% sodium hydroxide. The ether layer was separated, dried ($MgSO_4$), and evaporated, and produced a crystalline solid (314 mg, 95% crude yield). A recrystallization from carbon tetrachloride produced white crystals (310 mg, 93% overall), m.p. 60-61°, lit. (51) 61-62°. Infra-red spectrum ($CHCl_3$): included peaks at 1588 (m), 1486 (s), 1370 (m), 1171 (s), 1146 (vs), 971 (s), and 897 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): δ 3.15 (3 H, singlet), 7.40 (5 H, multiplet).

16. Preparation of Methane-d_3-sulfonyl Chloride

The hydrogens of methanesulfonyl chloride are extensively exchanged when it is reacted with 1,4-diazabicyclo-[2,2,2,]octane (DABCO) in the presence of deuterium oxide. The sulfonic acid product, when chlorinated with thionyl chloride, gave methanesulfonyl chloride with a deuterium content of approx. 80 atom %. The detailed procedure may be found in section IV B of the Experimental.

The product described above may be treated in the same way as the natural abundance material to obtain a product further enriched in deuterium. This product was found by its mass spectrum to be approx. 95 atom % deuterium.

A third treatment (overall yield very low) produced

almost pure trideuterated methanesulfonyl chloride. Refrative index, n_D^{25} 1.4543 (natural abundance n_D^{25} 1.4495). Infrared spectrum (CCl_4): the C-D stretch bands appeared at 2282, 2264, and 2140 cm^{-1}. The spectrum also included peaks at 1382 (vs), 1230 (m), 1181 (vs), 1022 (m), 940 (w), and 710 cm^{-1} (s). A deuterium analysis was done using the peaks at *m/e* 79, 80, 81, 82, 83, 84, and 85 (CH_3SO_2+) in the mass spectrum. Relative peak heights were 0, 0, 5.7, 100, 7.2, 4.7, and 3.9, respectively. The composition of the sample was calculated to be:

Methyl Group	Mole %
CH_3	0
CH_2D	0
CHD_2	5.4
CD_3	94.7

The above composition corresponds to a deuterium content of 98.2 mole %.

III. KINETICS

Kinetic experiments were done on methanesulfonyl chloride (usually .001 or .002*M*) and various bases and traps in 1,2-dimethoxyethane. Two temperatures were used, -25°C and +20°C. The low temperature runs were conducted by

precooling 25.0 ml samples of the sulfonyl chloride solution, and the solution containing the base and the traps, in the ethanol bath of a Gebrüder Haake Model KT-62 constant temperature bath maintained at -25.0 ± 0.2°. After 10 min the required temperature had been attained, and the solutions were quickly mixed. After an appropriate length of time, the reaction was stopped by the addition of 35% nitric acid (1.0 ml unless otherwise stated). Reactions were generally followed to about two-thirds completion. Chloride was determined using standard silver nitrate solution, and the titration was followed potentiometrically. The procedure has been described in detail by Lee (15).

The runs at 20° were done in a conventional water bath kept at 20.0 ± 0.1 °. A 25.0 ml sample of the sulfonyl chloride solution was thermostatted for 10 min, and to it was pipetted a 25.0 ml sample of thermostatted base/trap solution. Otherwise the procedure was as already described for the low temperature runs.

The concentration of unreacted sulfonyl chloride c was calculated from the silver nitrate titer. In all cases the base was in large excess, and pseudo-first-order rate plots were obtained when the log of concentration was plotted against time. All runs produced good straight lines, and k_{obs} (the pseudo-first-order rate constant) was obtained from the slope (in sec^{-1}) x 2.303. The second-order rate constant, k_2, is given where applicable, and was calculated from k_{obs} by dividing by the base concentration.

A. Methanesulfonyl Chloride and Tertiary Bases at -25°C

Kinetics of Methanesulfonyl Chloride and Quinuclidine

$$[CH_3SO_2Cl]_0 = 2.095 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 4.02 \times 10^{-2} M$$

Temperature: - 25.0°C.

Solutions: Methanesulfonyl chloride, 244 mg in 250 ml ($4.26 \times 10^{-3} M$); quinuclidine, 2.235 g in 250 ml ($8.04 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.095	-2.679
0.13	9.07	1.188	-2.925
0.19	11.15	.980	-3.009
0.25	13.23	.772	-3.112
0.35	15.28	.567	-3.246
1.00	20.43	.052	-4.284

$$k_{obs} = 5.66 \times 10^{-2}\ \text{sec}^{-1}$$
$$k_2 = 1.41\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and 1,4-Diazabicyclo-[2,2,2]octane (DABCO)

$$[CH_3SO_2Cl]_0 = 1.960 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 2.00 \times 10^{-2} M$$

Temperature: -25.0°C.

Solutions: Methanesulfonyl chloride, 266 mg in 500 ml ($3.95 \times 10^{-3} M$); DABCO, 1.122 g in 250 ml ($4.00 \times 10^{-2} M$). Titrated with $1.00 \times 10^{-2} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.960	-2.708
0.50	1.93	1.574	-2.803
1.00	3.44	1.272	-2.895
1.50	4.61	1.038	-2.984
2.00	5.46	.868	-3.062
2.50	6.21	.718	-3.144

$$k_{obs} = 6.74 \times 10^{-3}\ \text{sec}^{-1}$$

$$k_2 = 3.38 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and DABCO

$$[CH_3SO_2Cl]_0 = 2.133 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 1.99 \times 10^{-2} M$$

Temperature: -25.0°C.

Solutions: Methanesulfonyl chloride, 123 mg in 250 ml ($4.28 \times 10^{-3} M$); DABCO, 2.236 g in 500 ml ($3.985 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.133	-2.671
0.50	4.14	1.719	-2.765
1.00	7.71	1.362	-2.865
1.49	10.02	1.131	-2.947
2.00	12.17	.916	-3.038
2.50	14.10	.723	-3.141

$$k_{obs} = 7.10 \times 10^{-3}\ \text{sec}^{-1}$$
$$k_2 = 3.54 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

This experiment used the same DABCO solution as in the methane-d_3-sulfonyl chloride experiment in Section C.

Kinetics of Methanesulfonyl Chloride and DABCO

$$[CH_3SO_2Cl]_0 = 0.983 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 9.97 \times 10^{-3} M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 226 mg in 500 ml ($3.95 \times 10^{-3} M$); DABCO, 0.559 g in 250 ml ($1.994 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.983	-3.008
0.75	1.59	.824	-3.084
1.50	2.72	.711	-3.148
2.50	3.94	.589	-3.230
3.50	4.96	.487	-3.312
5.00	6.15	.368	-3.434

$$k_{obs} = 3.19 \times 10^{-3}\ \text{sec}^{-1}$$
$$k_2 = 3.20 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and DABCO

$$[CH_3SO_2Cl]_0 = 2.024 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 4.00 \times 10^{-2} M$$

Temperature: -25.0°C.

Solutions: Methanesulfonyl chloride, 226 mg in 500 ml ($3.95 \times 10^{-3} M$); DABCO, 2.243 g in 250 ml ($8.00 \times 10^{-2} M$). Titrated with $1.00 \times 10^{-2} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.024	-2.693
0.39	2.84	1.446	-2.840
0.80	4.86	1.052	-2.978
1.20	6.23	.778	-3.109
1.50	6.93	.638	-3.195

$$k_{obs} = 1.31 \times 10^{-2}\ \text{sec}^{-1}$$
$$k_2 = 3.26 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and Trimethylamine

$[CH_3SO_2Cl]_0 = 2.064 \times 10^{-3} M$

$[\ \text{Base}\ ] = 3.87 \times 10^{-2} M$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 237 mg in 500 ml ($4.138 \times 10^{-3} M$); trimethylamine, 2.5 ml in 500 ml ($7.748 \times 10^{-2} M$). The concentration of the amine was found by adding a known quantity of standard hydrochloric acid and back-titrating with standard sodium hydroxide. The solution was stored at $0^{\circ}C$ to avoid loss of the volatile amine. From time to time the concentration was checked by titration; little change was found. Chloride was determined by titration with $1.00 \times 10^{-2} M$ $AgNO_3$.

Time (ml)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.064	-2.685
0.51	0.71	1.922	-2.716
2.00	2.75	1.514	-2.820
4.00	3.49	1.366	-2.865
6.50	4.33	1.198	-2.922
10.0	5.36	.992	-3.003
14.0	6.40	.784	-3.106
20.5	7.69	.526	-3.279

$k_{obs} = 9.28 \times 10^{-4}\ sec^{-1}$

$k_2 = 2.40 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride and N,N-*Dimethylethylamine*

$$[CH_3SO_2Cl]_0 = 2.064 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 3.55 \times 10^{-2} M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 237 mg in 500 ml ($4.138 \times 10^{-3} M$); dimethylethylamine, 1.436 g in 250 ml ($7.096 \times 10^{-2} M$). The amine concentration was determined by addition of standard hydrochloric acid and back-titrating with standard sodium hydroxide solution, as described for trimethylamine. Chloride was determined with $1.00 \times 10^{-2} M$ standard $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.064	-2.685
4.00	1.76	1.712	-2.766
8.00	3.03	1.458	-2.836
12.00	4.04	1.256	-2.901
17.00	5.15	1.044	-2.981

$$k_{obs} = 6.52 \times 10^{-4}\ \text{sec}^{-1}$$
$$k_2 = 1.84 \times 10^{-2}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and N-*Methyldiethylamine*

$$[CH_3SO_2Cl]_0 = 2.085 \times 10^{-3}M$$
$$[\ \text{Base}\ ] = 3.98 \times 10^{-2}M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 244 mg in 500 ml ($4.264 \times 10^{-3}M$); methyldiethylamine, 1.735 g in 250 ml ($7.96 \times 10^{-2}M$). Titrated with $1.00 \times 10^{-2}M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	2.085	-2.681
3.05	1.73	1.739	-2.760
6.00	3.07	1.471	-2.832
10.00	4.50	1.186	-2.926
15.00	5.90	.905	-3.043
20.51	6.96	.692	-3.160

$$k_{obs} = 9.03 \times 10^{-4}\ \text{sec}^{-1}$$
$$k_2 = 2.27 \times 10^{-2}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and Triethylamine

$$[CH_3SO_2Cl]_0 = 2.101 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 4.01 \times 10^{-2} M$$

Temperature: -25.0°C.

Solutions: Methanesulfonyl chloride, 123 mg in 250 ml ($4.304 \times 10^{-3} M$); triethylamine, 4.062 g in 500 ml ($8.028 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.101	-2.677
2.00	2.98	1.803	-2.744
4.00	5.42	1.559	-2.807
6.00	7.33	1.368	-2.864
8.00	9.24	1.177	-2.929
10.00	10.85	1.016	-2.993
12.00	12.10	.891	-3.050

$$k_{obs} = 1.19 \times 10^{-3}\ \text{sec}^{-1}$$
$$k_2 = 2.97 \times 10^{-2}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and N,N-*Diisopropylethylamine*

$$[CH_3SO_2Cl]_0 = 2.216 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 3.99 \times 10^{-2} M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 129 mg in 250 ml ($4.46 \times 10^{-3} M$); diisopropylethylamine, 5.159 g in 500 ml ($7.98 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.216	-2.654
21.0	4.91	1.725	-2.763
30.0	6.56	1.560	-2.807
40.0	8.28	1.388	-2.858
60.0	11.20	1.096	-2.960
80.0	13.43	.873	-3.059

$$k_{obs} = 1.95 \times 10^{-4}\ \text{sec}^{-1}$$
$$k_2 = 4.90 \times 10^{-3}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and Tributylamine

$$[CH_3SO_2Cl]_0 = 2.102 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 4.01 \times 10^{-2} M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 244 mg in 500 ml ($4.264 \times 10^{-3} M$); tributylamine, 3.71 g in 250 ml ($8.01 \times 10^{-2} M$). Titrated with $1.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.102	-2.677
30.0	1.40	1.823	-2.739
60.0	2.54	1.595	-2.797
120.0	4.35	1.232	-2.909
180.0	5.82	.939	-3.027
240.0	6.86	.730	-3.137

$$k_{obs} = 7.43 \times 10^{-5}\ \text{sec}^{-1}$$

$$k_2 = 1.85 \times 10^{-3}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and N-*Methylmorpholine*

$$[CH_3SO_2Cl]_0 = 2.102 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 4.01 \times 10^{-2} M$$

Temperature: $-25.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 244 mg in 500 ml ($4.264 \times 10^{-3} M$); *N*-methylmorpholine, 2.028 g in 250 ml ($8.01 \times 10^{-2} M$). Titrated with $1.00 \times 10^{-2} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	2.102	-2.677
620	1.57	1.789	-2.748
1434	3.21	1.460	-2.836
2328	4.53	1.197	-2.922
2921	5.50	1.002	-2.999

$$k_{obs} = 4.18 \times 10^{-6}\ \text{sec}^{-1}$$

$$k_2 = 1.04 \times 10^{-4}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

B. Methanesulfonyl Chloride and Tertiary Bases at 20°C

Kinetics of Methanesulfonyl Chloride and Triethylamine

$$[CH_3SO_2Cl]_0 = 1.003 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 4.00 \times 10^{-2} M$$

Temperature: +20.0°C.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($2.04 \times 10^{-3} M$); triethylamine, 2.022 g in 250 ml ($8.00 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.003	-2.998
0.50	2.47	.756	-3.122
0.75	3.44	.659	-3.181
1.00	4.27	.576	-3.239
1.50	5.66	.437	-3.359
2.00	6.66	.337	-3.473

$$k_{obs} = 8.89 \times 10^{-3}\ \text{sec}^{-1}$$
$$k_2 = 2.22 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and Diisopropylethylamine

$$[CH_3SO_2Cl]_0 = 1.099 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 3.98 \times 10^{-2} M$$

Temperature: $+20.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 63.8 mg in 250 ml ($2.226 \times 10^{-3} M$); diisopropylethylamine, 1.028 g in 100 ml ($7.95 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.099	-2.959
2.00	1.95	.904	-3.044
5.00	4.28	.671	-3.173
8.00	6.04	.495	-3.305

$$k_{obs} = 1.65 \times 10^{-3}\ sec^{-1}$$

$$k_2 = 4.17 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride and Tributylamine

$$[CH_3SO_2Cl]_0 = 1.035 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 4.00 \times 10^{-2} M$$

Temperature: $+20.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 121 mg in 500 ml ($2.112 \times 10^{-3} M$); tributylamine, 3.709 g in 250 ml ($8.00 \times 10^{-2} M$). Titrated with $4.973 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.035	-2.985
4.18	2.35	.806	-3.094
8.20	3.92	.650	-3.187
12.17	5.18	.525	-3.280
16.50	6.13	.430	-3.366
21.29	7.08	.336	-3.474
28.67	8.06	.238	-3.623
39.07	8.99	.146	-3.830

$$k_{obs} = 8.45 \times 10^{-4}\ \text{sec}^{-1}$$
$$k_2 = 2.11 \times 10^{-2}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride and N-*Methylmorpholine*

$$[CH_3SO_2Cl]_0 = 1.104 \times 10^{-3} M$$
$$[\ \text{Base}\ ] = 3.99 \times 10^{-2} M$$

Temperature: $+20.0^{\circ}C$.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($2.04 \times 10^{-3} M$); *N*-methylmorpholine, 2.019 g in 250 ml ($7.983 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.014	-2.994
15.0	0.76	.938	-3.028
33.0	1.45	.869	-3.061
71.0	2.80	.734	-3.134
120.0	4.20	.594	-3.226
180.0	5.53	.461	-3.336
250.0	6.79	.335	-3.475

$$k_{obs} = 7.30 \times 10^{-5}\ \text{sec}^{-1}$$
$$k_2 = 1.82 \times 10^{-3}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

C. Methane-d_3-sulfonyl Chloride and Tertiary Bases at -25°C

Kinetics of Methane-d_3-sulfonyl Chloride and DABCO

$$[CD_3SO_2Cl]_0 = 1.910 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 1.99 \times 10^{-2} M$$

Temperature: -25°C.

Solutions: Methanesulfonyl chloride, 114 mg in 250 ml ($3.88 \times 10^{-3} M$); DABCO, 2.236 g in 500 ml ($3.985 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.910	-2.719
0.50	3.86	1.524	-2.817
1.00	6.66	1.244	-2.905
1.50	9.21	.989	-3.005
2.00	11.06	.804	-3.095
2.50	12.63	.647	-3.189

$$k_{obs} = 7.24 \times 10^{-3}\ \text{sec}^{-1}$$

$$k_2 = 3.62 \times 10^{-1}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

Kinetics of Methane-d_3-sulfonyl Chloride and Triethylamine

$$[CD_3SO_2Cl]_0 = 1.924 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 4.01 \times 10^{-2} M$$

Temperature: -25.0° C.

Solutions: Methanesulfonyl chloride, 113 mg in 250 ml ($3.848 \times 10^{-3} M$); triethylamine, 4.062 g in 500 ml ($8.03 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.924	-2.716
4.00	4.41	1.483	-2.828
6.00	6.13	1.311	-2.872
8.00	7.64	1.160	-2.935
10.00	9.08	1.016	-2.993
12.00	10.28	.896	-3.048
16.00	12.19	.705	-3.152

$$k_{obs} = 1.06 \times 10^{-3} \text{ sec}^{-1}$$

$$k_2 = 2.63 \times 10^{-2} \text{ 1 mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methane-d_3-sulfonyl Chloride, Triethylamine, and Water

$$[CD_3SO_2Cl] = 1.939 \times 10^{-3}M$$
$$[\ \text{Base}\ ] = 3.986 \times 10^{-2}M$$
$$[\ \text{Water}\ ] = 2.00 \times 10^{-1}M$$

Temperature: -25°C.

Solutions: Methanesulfonyl Chloride, 111.0 mg in 250 ml ($3.878 \times 10^{-3}M$); triethylamine, 2.016 g in 250 ml ($7.97 \times 10^{-2}M$); water, 1.800 g in the triethylamine solution ($4.00 \times 10^{-1}M$). Titrated with $5.00 \times 10^{-3}M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.929	-2.715
4.00	4.52	1.477	-2.831
6.00	6.32	1.297	-2.887
8.00	7.95	1.134	-2.945
12.00	10.52	.877	-3.057

$$k_{obs} = 1.09 \times 10^{-3}\ \text{sec}^{-1}$$
$$k_{obs}/[\text{Base}] = 2.74 \times 10^{-2}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

When this experiment was repeated using natural abundance methanesulfonyl chloride, $k_{obs}/[\text{Base}]$ was found to be 3.26×10^{-2} l mole^{-1} sec.$^{-1}$.

Kinetics of Methane-d_3-sulfonyl Chloride and Diisopropylethylamine

$$[CD_3SO_2Cl]_0 = 1.938 \times 10^{-3} M$$

$$[\ \text{Base}\ ] = 3.99 \times 10^{-3} M$$

Temperature: -25.0°C.

Solutions: Methanesulfonyl chloride, 88.8 mg in 200 ml ($3.878 \times 10^{-3} M$); diisopropylethylamine, 5.158 g in 500 ml ($7.98 \times 10^{-2} M$). Titrated with $5.00 \times 10^{-3} M$ standard $AgNO_3$.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.938	-2.713
20.0	3.32	1.606	-2.794
40.0	6.14	1.324	-2.878
60.0	8.15	1.123	-2.949
80.0	9.65	.973	-3.027
100.0	11.47	.791	-3.102

$$k_{obs} = 1.50 \times 10^{-4}\ \text{sec}^{-1}$$

$$k_2 = 3.77 \times 10^{-3}\ \text{l mole}^{-1}\ \text{sec}^{-1}$$

D. Methanesulfonyl Chloride and Tributylamine with Various Traps, at 20°C

Kinetics of Methanesulfonyl Chloride, Tributylamine, and N,N-*Dimethyl*-p-*phenylenediamine*

$$[CH_3SO_2Cl]_0 = 1.009 \times 10^{-3} M$$

$$[\ Bu_3N\ ] = 4.02 \times 10^{-2} M$$

$$[\ Trap\ ] = 2.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($2.050 \times 10^{-3} M$); Base solution: tributylamine, 3.722 g ($8.04 \times 10^{-2} M$) and *N,N*-dimethyl-*p*-phenylenediamine, 13.621 g ($4.00 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.009	-2.996
1.00	1.55	.854	-3.068
2.00	2.85	.724	-3.140
3.00	3.89	.620	-3.208
4.00	4.84	.525	-3.280
5.00	5.48	.461	-3.336
6.00	6.08	.401	-3.397

$$k_{obs} = 2.74 \times 10^{-3}\ sec^{-1}$$

$$k_{obs}/[Bu_3N] = 6.80 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Phenylenediamine

$$[CH_3SO_2Cl]_0 = 0.958 \times 10^{-3} M$$

$$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$$

$$[\ Trap\ ] = 1.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.983 \times 10^{-3} M$); Base solution: tributylamine, 3.707 g ($8.01 \times 10^{-2} M$) and *p*-phenylenediamine, 5,433 g ($2.009 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.958	-3.018
1.00	1.45	.813	-3.090
2.00	2.82	.676	-3.170
4.00	4.79	.479	-3.320
6.00	6.21	.337	-3.472

$$k_{obs} = 2.98 \times 10^{-3} \text{ sec}^{-1}$$

$$k_{obs}/[Bu_3N] = 7.45 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Phenylenediamine

$$[CH_3SO_2Cl]_0 = 0.981 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 2.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.985 \times 10^{-3} M$); Base solution: tributylamine, 3.713 g ($8.01 \times 10^{-2} M$) and *p*-phenylenediamine, 10.818 g ($4.00 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.981	-3.008
0.50	1.53	.828	-3.082
1.00	2.73	.708	-3.150
2.00	4.57	.524	-3.281
3.00	5.95	.386	-3.413
4.00	6.77	.304	-3.517

$$k_{obs} = 5.13 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 1.28 \times 10^{-1}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Anisidine

$[CH_3SO_2Cl]_0 = 1.002 \times 10^{-3} M$

$[\ Bu_3N\ ] = 3.93 \times 10^{-2} M$

$[\ Trap\ ] = 2.04 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 116 mg in 500 ml ($2.034 \times 10^{-3} M$); Base solution: tributylamine, 3.708 g ($7.86 \times 10^{-2} M$) and *p*-anisidine, 12.758 g ($4.07 \times 10^{-1} M$) in 254 ml of solution. Reaction was stopped with 210 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.002	-2.999
2.00	1.80	.822	-3.085
4.00	3.23	.679	-3.168
6.00	4.37	.565	-3.248
8.00	5.31	.471	-3.327
11.00	6.40	.362	-3.442

$k_{obs} = 1.55 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 3.96 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Anisidine

$$[CH_3SO_2Cl]_0 = 1.140 \times 10^{-3}M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2}M$$
$$[\ Trap\ ] = 4.00 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 66.4 mg in 250 ml ($2.31 \times 10^{-3}M$); Base solution: tributylamine, 3.703 g ($7.99 \times 10^{-2}M$) and *p*-anisidine, 24.641 g ($8.00 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.140	-2.943
1.00	1.57	.983	-3.007
2.00	2.85	.855	-3.068
4.00	4.79	.661	-3.180
6.00	6.25	.515	-3.288
10.00	8.25	.315	-3.524

$$k_{obs} = 2.24 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 5.60 \times 10^{-2}\ 1\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Toluidine

$$[CH_3SO_2Cl]_0 = 0.986 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$$
$$[\ Trap\ ] = 1.99 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.991 \times 10^{-3} M$); Base solution: tributylamine, 3.703 g ($7.992 \times 10^{-2} M$) and *p*-toluidine, 10.667 g ($3.98 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 3.0 ml of 35% HNO_3. Titrated with $4.973 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.968	-3.015
2.02	1.48	.821	-3.086
4.07	2.74	.696	-3.158
6.09	3.72	.598	-3.224
8.00	4.59	.512	-3.291
12.00	5.91	.380	-3.420
18.00	7.27	.245	-3.611

$$k_{obs} = 1.31 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.27 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Toluidine

$$[CH_3SO_2Cl]_0 = 0.986 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 3.99 \times 10^{-2} M$$
$$[\ Trap\ ] = 3.99 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.991 \times 10^{-3} M$); Base solution: tributylamine, 3.703 g ($7.99 \times 10^{-2} M$) and *p*-toluidine, 21.399 g ($7.99 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $4.973 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.986	-3.006
2.00	2.10	.777	-3.109
4.00	3.48	.640	-3.194
6.03	4.62	.527	-3.279
9.02	5.95	.394	-3.405
19.98	8.45	.146	-3.838

$$k_{obs} = 1.71 \times 10^{-3} \text{ sec}^{-1}$$
$$k_{obs}/[Bu_3N] = 4.27 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and Aniline

$[CH_3SO_2Cl]_0 = 1.109 \times 10^{-3} M$

$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$

$[\ Trap\ ] = 2.00 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 129 mg in 500 ml ($2.246 \times 10^{-3} M$); Base solution: tributylamine, 3.715 g ($8.016 \times 10^{-2} M$) and aniline, 9.305 g ($3.997 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.109	-2.955
2.50	2.02	.907	-3.042
5.00	3.64	.745	-3.128
7.00	4.66	.643	-3.192
9.00	5.57	.552	-3.258
11.00	6.33	.476	-3.322

$k_{obs} = 1.25 \times 10^{-3}$ sec^{-1}

$k_{obs}/[Bu_3N] = 3.12 \times 10^{-2}$ l mole^{-1} sec^{-1}

Kinetics of Methanesulfonyl Chloride, Tributylamine, and Aniline

$$[CH_3SO_2Cl]_0 = 1.071 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 4.01 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 61.8 mg in 250 ml ($2.158 \times 10^{-3} M$); Base solution: tributylamine, 3.710 g ($8.02 \times 10^{-2} M$) and aniline, 18.681 g ($8.02 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.071	-2.970
2.00	2.00	.871	-3.060
4.00	3.49	.722	-3.141
7.02	5.17	.553	-3.257
10.00	6.48	.423	-3.374
13.00	7.58	.313	-3.504

$$k_{obs} = 1.58 \times 10^{-3} \text{ sec}^{-1}$$
$$k_{obs}/[Bu_3N] = 3.94 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Anisidine*

$$[CH_3SO_2Cl]_0 = 1.011 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 2.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($2.05 \times 10^{-3} M$); Base solution: tributylamine, 3.712 g ($8.01 \times 10^{-2} M$) and *m*-anisidine, 12.327 g ($4.01 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.011	-2.995
2.00	1.66	.845	-3.073
4.00	2.95	.716	-3.145
6.00	4.06	.605	-3.218
8.00	4.98	.513	-3.290
10.00	5.74	.437	-3.360
12.00	6.40	.371	-3.431

$$k_{obs} = 1.41 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.52 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Anisidine*

$$[CH_3SO_2Cl]_0 = 1.036 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$$
$$[\ Trap\ ] = 4.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 60.5 mg in 250 ml ($2.114 \times 10^{-3} M$); Base solution: tributylamine, 3.706 g ($8.01 \times 10^{-2} M$) and *m*-anisidine, 24.643 g ($8.00 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.036	-2.985
2.00	2.12	.824	-3.084
4.00	3.68	.668	-3.175
6.00	4.91	.545	-3.264
8.00	5.91	.445	-3.352
10.00	6.74	.362	-3.441
13.00	7.66	.270	-3.568

$$k_{obs} = 1.76 \times 10^{-3} \text{ sec}^{-1}$$
$$k_{obs}/[Bu_3N] = 4.39 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Chloroaniline

$$[CH_3SO_2Cl]_0 = 1.200 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 0.786 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 68.6 mg in 250 ml ($2.400 \times 10^{-3} M$); Base solution: tributylamine, 3.715 g ($8.01 \times 10^{-2} M$) and *p*-chloroaniline, 5.006 g ($1.571 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.200	-2.921
2.00	1.53	1.047	-2.980
4.00	2.82	.918	-3.037
7.00	4.43	.757	-3.121
8.50	5.16	.684	-3.165
10.00	5.72	.628	-3.202
13.00	6.82	.518	-3.286

$$k_{obs} = 1.08 \times 10^{-3} \text{ sec}^{-1}$$
$$k_{obs}/[Bu_3N] = 2.69 \times 10^{-2} \text{ l mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Chloroaniline

$$[CH_3SO_2Cl]_0 = 1.047 \times 10^{-3}M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2}M$$
$$[\ Trap\ ] = 2.00 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 121 mg in 500 ml ($2.122 \times 10^{-3}M$); Base solution: tributylamine, 3.711 g ($8.02 \times 10^{-2}M$) and *p*-chloroaniline, 12.765 g ($4.00 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.047	-2.980
2.00	1.79	.868	-3.062
5.00	3.78	.669	-3.175
8.00	5.27	.520	-3.284
11.00	6.42	.405	-3.392

$$k_{obs} = 1.43 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.58 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Chloroaniline

$$[CH_3SO_2Cl]_0 = 1.066 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 2.01 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 124 mg in 500 ml ($2.163 \times 10^{-3} M$); Base solution: tributylamine, 3.715 g ($8.02 \times 10^{-2} M$) and *p*-chloroaniline, 12.806 g ($4.02 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.066	-2.973
2.00	1.58	.908	-3.042
4.00	2.84	.782	-3.107
6.00	3.93	.673	-3.172
8.00	4.87	.579	-3.237
11.00	6.05	.461	-3.337

$$k_{obs} = 1.26 \times 10^{-3} \text{ sec}^{-1}$$
$$k_{obs}/[Bu_3N] = 3.14 \times 10^{-2} \text{ 1 mole}^{-1} \text{ sec}^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Chloroaniline

$$[CH_3SO_2Cl]_0 = 1.002 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 3.10 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($2.034 \times 10^{-3} M$); Base solution: tributylamine, 3.712 g ($8.01 \times 10^{-2} M$) and *p*-chloroaniline, 19.769 g ($6.20 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 3.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.002	-2.999
2.00	1.63	.839	-3.076
4.00	2.95	.707	-3.151
5.77	3.98	.605	-3.218
9.00	5.42	.460	-3.337
12.00	6.46	.356	-3.449

$$k_{obs} = 1.44 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.60 \times 10^{-2}\ 1\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Chloroaniline

$[CH_3SO_2Cl]_0 = 1.109 \times 10^{-3}M$

$[\ Bu_3N\ ] = 4.015 \times 10^{-2}M$

$[\ Trap\ ] = 4.01 \times 10^{-1}M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 129 mg in 500 ml ($2.246 \times 10^{-3}M$); Base solution: tributylamine, 3.720 g ($8.03 \times 10^{-2}M$) and *p*-chloroaniline, 25.521 g ($8.01 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.109	-2.955
2.00	2.25	.884	-3.054
4.00	3.93	.716	-3.145
5.50	5.01	.608	-3.216
7.00	5.85	.524	-3.281
9.00	6.83	.426	-3.371

$k_{obs} = 1.73 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 4.31 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine and p-Chloroaniline

$$[CH_3SO_2Cl]_0 = 0.936 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$$
$$[\ Trap\ ] = 4.08 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 228 mg in 1000 ml ($1.991 \times 10^{-3} M$); Base solution: tributylamine, 3.714 g ($8.02 \times 10^{-2} M$) and *p*-chloroaniline, 26.004 g ($8.155 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	0.936	-3.029
2.00	1.82	.754	-3.123
4.01	3.25	.611	-3.214
7.00	4.83	.453	-3.344
10.00	6.00	.336	-3.474
14.01	7.08	.228	-3.642

$$k_{obs} = 1.72 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 4.30 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-Chloroaniline

$[CH_3SO_2Cl]_0 = 1.014 \times 10^{-3} M$

$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$

$[\ Trap\ ] = 1.99 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 118 mg in 500 ml ($2.055 \times 10^{-3} M$); Base solution: tributylamine, 3.711 g ($8.01 \times 10^{-2} M$) and *m*-chloroaniline, 12.763 g ($3.972 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.014	-2.994
2.00	1.38	.876	-3.058
4.00	2.57	.757	-3.121
7.00	4.01	.613	-3.213
10.00	5.16	.498	-3.303
14.00	6.36	.378	-3.423

$k_{obs} = 1.17 \times 10^{-3}$ sec^{-1}

$k_{obs}/[Bu_3N] = 2.94 \times 10^{-2}$ l mole^{-1} sec^{-1}

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Chloroaniline*

$$[CH_3SO_2Cl]_0 = 1.085 \times 10^{-3}M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2}M$$
$$[\ Trap\ ] = 4.00 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 63.6 mg in 250 ml ($2.223 \times 10^{-3}M$); Base solution: tributylamine, 3.702 g ($7.99 \times 10^{-2}M$) and *m*-chloroaniline, 25.519 g ($8.00 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.085	-2.965
2.00	1.85	.900	-3.046
4.00	3.37	.748	-3.126
6.00	4.63	.622	-3.206
8.00	5.68	.517	-3.286
10.00	6.52	.433	-3.364
13.00	7.51	.334	-3.476

$$k_{obs} = 1.53 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.83 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Nitroaniline*

$$[CH_3SO_2Cl]_0 = 1.014 \times 10^{-3}M$$

$$[\ Bu_3N\ ] = 4.00 \times 10^{-2}M$$

$$[\ Trap\ ] = 1.00 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 118 mg in 500 ml ($2.055 \times 10^{-3}M$); Base solution: tributylamine, 3.707 g ($8.00 \times 10^{-2}M$) and *m*-nitroaniline, 6.902 g ($2.00 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.014	-2.994
2.00	1.38	.876	-3.057
4.00	2.45	.769	-3.114
6.00	3.38	.676	-3.170
10.00	4.99	.515	-3.288
15.00	6.39	.375	-3.426

$$k_{obs} = 1.11 \times 10^{-3}\ sec^{-1}$$

$$k_{obs}/[Bu_3N] = 2.77 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Nitroaniline*

$[CH_3SO_2Cl]_0 = 1.047 \times 10^{-3} M$

$[\ Bu_3N\ ] = 4.005 \times 10^{-2} M$

$[\ Trap\ ] = 2.00 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 121 mg in 500 ml ($2.122 \times 10^{-3} M$); Base solution: tributylamine, 3.711 g ($8.01 \times 10^{-2} M$) and *m*-nitroaniline, 13.835 g ($4.006 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.047	-2.980
2.00	1.98	.849	-3.071
4.00	3.39	.708	-3.150
6.00	4.56	.591	-3.228
8.00	5.52	.495	-3.305
10.00	6.41	.406	-3.391

$k_{obs} = 1.57 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 3.91 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Nitroaniline*

$$[CH_3SO_2Cl]_0 = 1.066 \times 10^{-3} M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$$
$$[\ Trap\ ] = 2.00 \times 10^{-1} M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 124 mg in 500 ml ($2.163 \times 10^{-3} M$); Base solution: tributylamine, 3.702 g ($7.99 \times 10^{-2} M$) and *m*-nitroaniline, 13.806 g ($4.00 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 1.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.066	-2.973
2.00	2.00	.866	-3.062
4.00	3.49	.717	-3.144
8.00	5.69	.497	-3.303

$$k_{obs} = 1.59 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 3.99 \times 10^{-2}\ 1\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-Nitroaniline

$[CH_3SO_2Cl]_0 = 1.050 \times 10^{-3}M$

$[\ Bu_3N\ ] = 4.01 \times 10^{-2}M$

$[\ Trap\ ] = 3.01 \times 10^{-1}M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 122 mg in 500 ml ($2.130 \times 10^{-3}M$); Base solution: tributylamine, 3.712 g ($8.01 \times 10^{-2}M$) and *m*-nitroaniline, 20.769 g ($6.014 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 1.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.050	-2.979
2.00	2.14	.836	-3.078
4.00	3.58	.692	-3.160
6.00	4.80	.570	-3.244
8.00	5.85	.465	-3.333
11.00	7.01	.349	-3.457

$k_{obs} = 1.63 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 4.06 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and m-*Nitroaniline*

$[CH_3SO_2Cl]_0 = 1.151 \times 10^{-3} M$

$[\ Bu_3N\ ] = 4.00 \times 10^{-2} M$

$[\ Trap\ ] = 4.04 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 65.9 mg in 250 ml ($2.302 \times 10^{-3} M$); Base solution: tributylamine, 3.706 g ($8.00 \times 10^{-2} M$) and *m*-nitroaniline, 27.869 g ($8.07 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.128	-2.948
2.00	2.77	.851	-3.070
4.00	4.14	.714	-3.146
6.00	5.75	.553	-3.257
8.00	6.62	.466	-3.338
10.00	7.59	.369	-3.433
13.00	8.45	.283	-3.548

$k_{obs} = 1.80 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 4.50 \times 10^{-2}\ 1\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Nitroaniline

$[CH_3SO_2Cl]_0 = 0.958 \times 10^{-3}M$

$[\ Bu_3N\ ] = 3.90 \times 10^{-2}M$

$[\ Trap\ ] = 1.95 \times 10^{-1}M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.983 \times 10^{-3}M$); Base solution: tributylamine, 3.708 g ($7.80 \times 10^{-2}M$) and *p*-nitroaniline, 13.814 g ($3.90 \times 10^{-1}M$) in 257 ml of solution. Reaction was stopped with 2.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	0.958	-3.018
2.00	1.59	.799	-3.098
4.00	2.90	.668	-3.175
6.00	3.97	.561	-3.251
8.00	4.90	.468	-3.330
11.00	5.98	.360	-3.444

$k_{obs} = 1.64 \times 10^{-3}$ sec $^{-1}$

$k_{obs}/[Bu_3N] = 4.22 \times 10^{-2}$ l mole^{-1} sec^{-1}

Kinetics of Methanesulfonyl Chloride, Tributylamine, and p-Nitroaniline

$[CH_3SO_2Cl]_0 = 1.153 \times 10^{-3}M$

$[\ Bu_3N\ ] = 4.00 \times 10^{-2}M$

$[\ Trap\ ] = 4.00 \times 10^{-1}M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 64.6 mg in 250 ml ($2.26 \times 10^{-3}M$); Base solution: tributylamine, 3.712 g ($8.00 \times 10^{-2}M$) and *p*-nitroaniline, 27.621 g ($8.00 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	1.153	-2.938
1.00	2.07	.946	-3.024
2.00	3.42	.811	-3.091
3.00	4.58	.695	-3.158
4.00	5.55	.598	-3.223
6.00	7.18	.435	-3.362

$k_{obs} = 2.60 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 6.50 \times 10^{-2}\ 1\ mole^{-1}\ sec^{-1}$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and Isopropyl Alcohol

$$[CH_3SO_2Cl]_0 = 0.986 \times 10^{-3}M$$
$$[\ Bu_3N\ ] = 3.99 \times 10^{-2}M$$
$$[\ Trap\ ] = 4.00 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.991 \times 10^{-3}M$); Base solution: tributylamine, 3.701 g ($7.99 \times 10^{-2}M$) and isopropyl alcohol, 12.004 g ($7.99 \times 10^{-1}M$) in 250 ml of solution. Reaction was stopped with 1.0 ml of 35% HNO_3. Titrated with $4.973 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	0.986	-3.006
4.03	2.21	.766	-3.115
8.04	3.88	.600	-3.222
12.00	5.14	.475	-3.323
17.03	6.39	.351	-3.455
25.14	7.73	.218	-3.661
35.59	8.72	.119	-3.924

$$k_{obs} = 1.01 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 2.53 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, and Isopropyl Alcohol

$$[CH_3SO_2Cl]_0 = 0.986 \times 10^{-3}M$$
$$[\ Bu_3N\ ] = 4.00 \times 10^{-2}M$$
$$[\ Trap\ ] = 8.25 \times 10^{-1}M$$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 114 mg in 500 ml ($1.991 \times 10^{-3}M$); Base solution: tributylamine, 3.703 g ($7.99 \times 10^{-2}M$) and isopropyl alcohol, 24.795 g (1.650*M*) in 250 ml of solution. Reaction was stopped with 1.0 ml of 35% HNO_3. Titrated with $4.973 \times 10^{-3}M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3}M$)	Log c
0	0	0.986	-3.006
4.00	2.51	.737	-3.133
8.00	4.31	.558	-3.254
12.00	5.68	.421	-3.376
17.03	6.90	.300	-3.523
25.00	8.14	.177	-3.752
35.00	8.99	.092	-4.036

$$k_{obs} = 1.19 \times 10^{-3}\ sec^{-1}$$
$$k_{obs}/[Bu_3N] = 2.97 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$$

Kinetics of Methanesulfonyl Chloride, Tributylamine, p-Toluidine, and Isopropyl Alcohol

$[CH_3SO_2Cl]_0 = 1.009 \times 10^{-3} M$

$[\ Bu_3N\ ] = 4.01 \times 10^{-2} M$

$[p\text{-toluidine}] = 3.92 \times 10^{-1} M$

$[2\text{-propanol}] = 3.94 \times 10^{-1} M$

Temperature: 20.0°C.

Solutions: Methanesulfonyl chloride, 117 mg in 500 ml ($1.023 \times 10^{-3} M$); Base solution: tributylamine, 3.712 g ($8.01 \times 10^{-2} M$), *p*-toluidine, 20.992 g ($7.84 \times 10^{-1} M$), and 2-propanol, 11.837 g ($7.88 \times 10^{-1} M$) in 250 ml of solution. Reaction was stopped with 4.0 ml of 35% HNO_3. Titrated with $5.00 \times 10^{-3} M$ $AgNO_3$ solution.

Time (min)	Titer (ml)	c ($10^{-3} M$)	Log c
0	0	1.009	-2.996
2.00	2.19	.790	-3.102
4.02	3.80	.629	-3.201
6.00	5.09	.500	-3.301
8.00	6.06	.403	-3.395
10.02	6.87	.322	-3.492
13.00	7.70	.239	-3.622

$k_{obs} = 1.91 \times 10^{-3}\ sec^{-1}$

$k_{obs}/[Bu_3N] = 4.78 \times 10^{-2}\ l\ mole^{-1}\ sec^{-1}$

IV. DEUTERIUM EXCHANGE EXPERIMENTS

A. Reaction of Methanesulfonyl Chloride with Quinuclidine and Deuterium Oxide

A solution containing quinuclidine (1.018 g, 9.17 mmole) and deuterium oxide (2.0 ml, 111 mmole) in dimethoxyethane (15 ml) was mixed with a solution of methanesulfonyl chloride (471 mg, 4.03 mmole) in 1,2-dimethyoxyethane (15 ml). The reaction mixture gradually became cloudy, and after a few minutes a small liquid phase had formed on the bottom. The reaction was allowed to stand at room temperature for 10 min, after which the solvent was evaporated under reduced pressure. The colourless oil that remained was placed as a concentrated aqueous solution on an ion exchange column, made up of 10 ml of wet Rexyn 101 (H) (Fisher R-204). The product was passed through the column using a minimum of water, and until the eluent no longer tested strongly acidic to pH paper.

The aqueous solution obtained above was evaporated on the water bath at 80° using a rotary evaporator. The sulfonic acid was obtained as a white oil, and was converted to the sulfonyl chloride by adding an excess of thionyl chloride, in dropwise fashion, to the stirred sulfonic acid at 95°. The addition took about 30 min, and the reaction was allowed to reflux for an additional 3 h.

The excess thionyl chloride was evaporated and the

sulfonyl chloride obtained (339 mg, 72%) was purified by a cold-finger distillation, b.p. 48°/10 mm. Infra-red spectrum (CCl_4): prominent peaks due to C-D stretching were present at 2284, 2265, and 2140 cm^{-1}. Other peaks were found at 1370 (vs), 1231 (m), 1175 (vs), 1015 (s), 911 (m), 860 (w), and 710 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): Multiplet at δ 3.67. The multiplet was interpreted as the superimposed spectra of several differently exchanged sulfonyl chlorides, and was more closely examined in the DABCO experiment. Mass spectrum: the parent ion peaks were observed at *m/e* 114-117. For the deuterium analysis it was found convenient to use the peaks at *m/e* 79-85, which correspond to CH_3SO_2+. It was demonstrated that no isotopic fractionation takes place on loss of chloride, and results taken from the *m/e* 79-85 region were the same as from the parent ion region. Relative peak intensities for *m/e* 79, 80, 81, 82, 83, 84 and 85 were 2.9, 20.5, 34.7, 100, 4.1, 4.7, and 0.8 respectively. Natural abundance methanesulfonyl chloride was found to have relative peak intensities of 100, 1.9, 4.6, and 0.2 for *m/e* 79, 80, 81, and 82. The proportions of the deuterated species were calculated, using the natural abundance values to correct for the M+1, M+2, and M+3 peaks. The results were:

Methyl Group	Mole %
CH_3	1.8
CH_2D	13.1
CHD_2	21.9
CD_3	63.1

B. Reaction of Methanesulfonyl Chloride with 1,4-Diazabicyclo[2,2,2]octane (DABCO) and Deuterium Oxide

The experiment was done as described for quinuclidine, with DABCO (18.30 g, 163.1 mmole) and deuterium oxide (40.0 ml, 2210 mmole) in dimethoxyethane (300 ml), and methanesulfonyl chloride (9.20 g, 80.3 mmole) in dimethoxyethane (300 ml). About 120 ml of wet ion exchange resin was used to generate the free sulfonic acid.

Treatment with thionyl chloride followed by distillation produced the sulfonyl chloride as a white liquid (2.528 g, 27%). Infra-red spectrum (CCl_4): C-D stretch absorptions were noted at 2285, 2265, and 2240 cm^{-1}. Other peaks included those at 1370 (vs), 1231 (m), 1175 (vs), 1022 (w), 968 (w), 910 (m), and 710 cm^{-1} (s). N.m.r. spectrum ($CDCl_3$): a multiplet at δ 3.72 was interpreted as consisting of a singlet, a 1:1:1 triplet (J = 2.0 Hz) shifted to higher field by about 0.016 p.p.m., and a 1:2:3:2:1 quintet (J = 1.9 Hz) shifted to higher field by another 0.016 p.p.m. A deuterium analysis was done using the *m/e* 79-85 region

of the mass spectrum. Relative intensities for *m/e* 79, 80, 81, 82, 83, 84, and 85 were 2.1, 26.4, 38.0, 100, 5.7, 44.0, and 1.3. These values show the following amounts of deuterated species to the present:

Methyl Group	Mole %
CH_3	1.3
CH_2D	16.1
CHD_2	22.8
CD_3	59.8

The above mixture of deuterated sulfonyl chlorides was calculated to have 80.4 atom % deuterium. A deuterium analysis by Nemeth gave a value of 77.50 atom % excess D.

In a separate experiment, an excess of methanesulfonyl chloride was used. The recovered starting material (42%) was distilled and examined for exchange. Mass spectrum: the peaks at *m/e* 79, 80, 81, and 82 had relative intensities of 100, 2.3, 4.8, and 0.9 respectively. This is very similar to natural abundance methanesulfonyl chloride, which is 100, 1.9, 4.6, and 0.2. The composition of the recovered material was calculated as:

Methyl Group	Mole %
CH_3	99.6
CH_2D	0.4
CHD_2	0
CD_3	0

The error in the value for CH_2D was estimated to be approximately 0.1 mole % or ± 25%. It may be noted that natural abundance methanesulfonyl chloride contains approximately 0.05% CH_2D.

C. Reaction of Methanesulfonyl Chloride with Trimethylamine and Deuterium Oxide

The experiment was done as described for quinuclidine, using trimethylamine (20.5 ml, 12.5 g, 211 mmole) and deuterium oxide (40.0 ml, 2210 mmole) in dimethoxyethane (300 ml), and methanesulfonyl chloride (9.16 g, 80.0 mmole) in dimethoxyethane (300 ml). The reaction product was percolated through approximately 160 ml of wet ion exchange resin.

Treatment with thionyl chloride and distillation produced a small quantity of methanesulfonyl chloride. Infrared spectrum (CCl_4): peaks due to C-D stretching were noted at 2285, 2267, and 2141 cm^{-1}. Other peaks were at 1370 (vs), 1231 (m), 1175 (vs), 1021 (m), 970 (w), 940 (m), and 710 cm^{-1} (s).

N.m.r. spectrum ($CDCl_3$): a multiplet at δ 3.63 was interpreted as a singlet at 3.65, a 1:1:1 triplet at 3.63 (J = 2.0 Hz) and a 1:2:3:2:1 quintet at 3.62 (J = 1.9 Hz). Mass spectrum: a deuterium analysis using the peaks at *m/e* 79, 80, 81, 82, 83, 84, and 85 gave relative intensities of 3.7, 51.6, 50.9, 100, 5.6, 4.8, and 0.9, respectively. These values indicate the following composition:

Methyl Group	Mole %
CH_3	1.8
CH_2D	25.6
CHD_2	24.7
CD_3	48.0

In a separate experiment, less than an excess of trimethylamine was used. Some starting material (5%) was recovered, and its n.m.r. spectrum examined. There was no evidence of exchange in the starting material, the spectrum exhibiting only a sharp singlet.

D. Reaction of Methanesulfonyl Chloride with *N,N*-Dimethylethylamine and Deuterium Oxide

The experiment was carried out as already described for quinuclidine, using dimethylethylamine (8.642 g, 118 mmole) and deuterium oxide (20.0 ml, 1110 mmole) in dimethoxyethane

(150 ml), and methanesulfonyl chloride (6.06 gm, 53.0 mmole) in dimethoxyethane (150 ml). The reaction product was percolated through about 120 ml of wet ion exchange resin.

Treatment with thionyl chloride and distillation gave the sulfonyl chloride (2.785 g, 46%). Mass spectrum: a deuterium analysis using the peaks at *m/e* 79, 80, 81, 82, 83, 84, and 85 gave relative peak intensities of 6.7, 100, 27.0, 13.8, 2.0, 0.5, and 0.6. This gives the following values:

Methyl Group	Mole %
CH_3	4.8
CH_2D	71.4
CHD_2	17.6
CD_3	6.2

The dimethylethylamine experiment was repeated using the same quantities of deuterium oxide and solvent, but using reduced quantities of dimethylethylamine (1.558 g, 21.3 mmole) and methanesulfonyl chloride (1.134 g, 9.91 mmole). Mass spectrum: the peaks at *m/e* 79, 80, 81, 82, 83, and 84 had relative intensities of 3.3, 100, 36.9, 20.3, 2.1, and 0.7. This gives the following composition:

Methyl Group	Mole %
CH_3	2.2
CH_2D	65.4
CHD_2	22.8
CD_3	9.7

E. Reaction of Methanesulfonyl Chloride with *N*-Methyldiethylamine and Deuterium Oxide

The experiment was carried out as described for quinuclidine, using methyldiethylamine (8.784 g, 101 mmole) and deuterium oxide (20.0 ml, 1110 mmole) in dimethoxyethane (150 ml), and methanesulfonyl chloride (4.60 g, 40.0 mmole) in dimethoxyethane (150 ml). The product was percolated through approximately 80 ml of wet ion exchange resin.

Treatment with thionyl chloride and distillation produced a small sample of the sulfonyl chloride. Mass spectrum: the peaks at *m/e* 79, 80, 81, 82, and 83 had relative intensities of 5.2, 100, 4.9, 5.5, and 1.3, respectively. These values give the following composition:

Methyl Group	Mole %
CH_3	4.8
CH_2D	92.0
CHD_2	2.5
CD_3	0.8

F. Reaction of Methanesulfonyl Chloride with Triethylamine and Deuterium Oxide

The experiment was carried out as for quinuclidine, using triethylamine (10.23 g, 101 mmole) and deuterium oxide (20.0 ml, 1110 mmole) in dimethoxyethane (150 ml), and methanesulfonyl chloride (4.60 g, 40 mmole) in dimethoxyethane (150 ml). Approximately 80 ml of wet ion exchange resin was used.

Treatment with thionyl chloride and distillation produced the sulfonyl chloride (2.311 g, 50%). Infra-red spectrum (CCl_4): weak peaks due to C-D stretching were noted at 2230 and 2210 cm^{-1}. Other peaks were at 1374 (vs), 1233 (m), 1170 (vs), and 940 cm^{-1} (m). N.m.r. spectrum ($CDCl_3$): δ 3.63 (1:1:1 triplet, J = 2.0 Hz). A small singlet appeared at 3.65, superimposed on the triplet. Mass spectrum: the peaks at *m/e* 79, 80, 81, 82, 83, and 84 had relative intensities of 10.7, 100, 3.0, 4.5, 1.2, and 0.4, respectively. These values give the following composition:

Methyl Group	Mole %
CH_3	9.6
CH_2D	89.8
CHD_2	0.5
CD_3	0.0

The error estimated for the CHD_2 figure was 0.15 mole %, or ± 30%.

G. Reaction of Ethanesulfonyl Chloride with Diazabicyclooctane and Deuterium Oxide

A solution of DABCO (9.492 g, 84.6 mmole) and deuterium oxide (20.0 ml, 1105 mmole) in dimethoxyethane (150 ml) was added to a solution of ethanesulfonyl chloride (5.139 g, 40.0 mmole) in dimethoxyethane (150 ml). Isolation of the sulfonic acid was as already described in the methanesulfonyl chloride experiment.

The sulfonic acid was converted to the sulfonyl chloride using phosphorus pentachloride in chloroform. The reaction took about 15 min. The reaction was cooled and ice added. An extraction with ether and water was carried out. The product was a somewhat discoloured liquid (4.023 g, 78%). A bulb-to-bulb distillation was done with a Büchi 453 oven (oven temperature 70-75°, 15 mm). A pure white product was obtained. N.m.r. spectrum: δ 1.51 (3 H, multiplet), 3.58 (0.9 H, quartet of 1:1:1 triplets, J_H = 7.4, J_D = 2.3 Hz). The multiplet at 1.51 was a doublet of 1:1:1 triplets, J_H = 7.4, J_D = 1.3 Hz). In addition, a multiplet was noted at 1.53 p.p.m., superimposed on the main structure. Mass spectrum: a deuterium analysis was done using the peaks at 93, 94, 95, 96, and 97 ($CH_3CH_2SO_2$+). The relative peak

intensities were 6.7, 100, 19.6, 5.1, and 1.2, respectively. Calculations gave the following composition of the sample:

Methylene Group	Mole %
CH_2	5.5
CHD	81.4
CD_2	13.1

H. Reaction of Methanesulfonyl Chloride with DABCO and Methanol-*d*

A solution of DABCO (3.661 g, 32.7 mmole) and methanol-*d* (CH_3OD) (14.040 g, 425 mmole) in dimethoxyethane (50 ml) was added to a solution of methanesulfonyl chloride (1.803 g, 15.8 mmole) in dimethoxyethane (60 ml). After about 30 sec a precipitate had formed. The reaction was allowed to stand for 10 min, after which the solvent was evaporated, ether added, and an extraction with water carried out. The ether layer was separated, dried, and evaporated. A low yield of methyl methanesulfonate was obtained. The product was distilled in a cold-finger apparatus (oil bath 100°, 15 mm). A small amount of a white liquid was obtained. N.m.r. spectrum ($CDCl_3$): δ 3.04 (0.7 H, multiplet), 3.90 (3 H, sharp singlet). The multiplet at 3.04 was similar to the one observed for the DABCO and deuterium oxide experiment. On the basis of the n.m.r. spectrum, the deuterium content

of the methyl group appears to be approximately 76 atom %. It was not found possible to obtain a satisfactory mass spectrum.

J. Exchange in a Cycloaddition Reaction, and Related Experiments

1. *Reaction of Methanesulfonyl Chloride with Triethylamine and an Enamine*

A solution containing 1-(2-methylpropenyl)pyrrolidine (2.512 g, 20.1 mmole) and triethylamine (3.001 g,) in dimethoxyethane (75 ml) was added to a solution of methanesulfonyl chloride (2.286 g, 20.0 g) in dimethoxyethane (75 ml). After standing at room temperature for 10 min, the solvent was evaporated off. Ether was added and an extraction with dilute hydrochloric acid carried out. The aqueous layer was separated and sodium carbonate added until alkaline. An oil separated out. An extraction with ether produced a solid (2.541 g, 63% yield).

A recrystallization from chloroform produced white crystals, m.p. 64.5-66° (lit. (52) 67-68°). Infra-red spectrum (CCl_4): included peaks at 1457 (m), 1314 (vs), 1204 (s), 1108 (s), and 909 cm^{-1} (m). N.m.r. spectrum: ($CDCl_3$): δ 1.52 (3 H, singlet), 1.58 (3 H, singlet), 1.80 (4 H, multiplet), 2.46 (4 H, multiplet), 2.80 (1 H, doublet

of doublets, J = 9.6 and 8.6 Hz), 3.92 (2 H, two closely spaced absorptions; J = 9.6 for the low-field absorption, J = 8.6 Hz for the absorption at 0.003 p.p.m. higher field).

2. Reaction of Methanesulfonyl Chloride with DABCO and an Enamine

A solution of 1-(2-methylpropenyl)pyrrolidine (2.528 g, 20.2 mmole) and DABCO (2.994 g, 26.7 mmole) in dimethoxyethane (75 ml) was added to a solution of methanesulfonyl chloride (2.297 g, 20.1 mmole) in dimethoxyethane (75 ml). A workup as in the previous experiment produced the adduct (2.128 g, 52% yield) as a white solid. A recrystallization gave a product with m.p. 65-66.5°, m.p. mixed with authentic adduct, 64.5-66°. The i.r. and n.m.r. spectra were identical with the adduct obtained in the previous experiment.

3. Reaction of Methanesulfonyl Chloride with DABCO and an Enamine, in the presence of Deuterium Oxide

A solution of DABCO (2.512 g, 22.4 mmole), 1-(2-methylpropenyl)pyrrolidine (6.260 g, 50.0 mmole), and deuterium oxide (1.00 ml, 55.3 mmole) in dimethoxyethane (75 ml) was added to a solution of methanesulfonyl chloride (2.292 g, 20.0 mmole) in dimethoxyethane (75 ml). After 30 sec the reaction was stopped with concentrated hydrochloric acid

(12.0 ml). The solvent was evaporated and ether and water added. An extraction was carried out with dilute hydrochloric acid. The aqueous layer was separated and sodium carbonate added until it was slightly alkaline. An extraction with ether was carried out. The ether layer was dried ($MgSO_4$) and evaporated, and found to contain the adduct as a white solid (1.763 g, 44% yield). It was recrystallized from chloroform, m.p. 65-66°. The product was identical to that obtained in the absence of deuterium oxide, except for exchanged hydrogens. N.m.r. spectrum ($CDCl_3$): δ 1.53 (3 H, singlet), 1.57 (3 H, singlet), 1.78 (4 H, multiplet), 2.45 (4 H, multiplet), 2.80 (1 H, multiplet) and 3.92 (1.3 H, multiplet). The multiplet at 2.80 consisted of a doublet of doublets, J = 9.6 and 8.6 Hz, plus what appeared to be a doublet of 1:1:1 triplets, J_H = 8.5. The spectrum was also run on the Varian HA 100 instrument, where the absorption at 3.9 p.p.m. integrated for 1.25 H.

The experiment was repeated without using concentrated hydrochloric acid to stop the reaction. The product (1.987 g, 49% yield) was identical to the above product. The absorption at 3.9 p.p.m. in the n.m.r. spectrum (HA 100) integrated for 1.25 H.

In a separate experiment, the reaction was repeated, but using the enamine adduct mole for mole in place of

methanesulfonyl chloride. The workup was exactly as in the previous experiments. The adduct was recovered as a white crystalline solid (100% yield). No evidence was found for any exchange when the multiplet at 3.9 p.p.m. was examined in the n.m.r. spectrum.

K. Reaction of Methanesulfonyl Chloride with Butylamine-d_2

The deuterated butylamine was prepared by dissolving natural abundance n-butylamine (40.5 ml) in anhydrous ether (500 ml). It was washed with several batches of deuterium oxide. The final batch of deuterium oxide was separated, and appeared to be 0.6% H, as shown by n.m.r. The deuterated amine was isolated by distillation. The n.m.r. spectrum revealed only a very small peak due to NHD at 1.33 p.p.m. The amount of H was very difficult to estimate, but may have been approximately 5%.

A solution of the deuterated amine (4.514 g, 60.2 mmole) in dimethoxyethane (11.5 ml) was mixed with a solution of methanesulfonyl chloride (369 mg, 3.22 mmole) in dimethoxyethane (11.5 ml). The reaction was allowed to stand at room temperature for 10 min, after which the solvent was evaporated and ether added. An extraction with dilute hydrochloric acid was carried out. The ether layer was found to contain a low-melting solid (468 mg, 96%). The product was distilled using a cold-finger apparatus (130°

bath temperature, 0.1 mm). N.m.r. spectrum ($CDCl_3$): δ 0.8 to 1.8 (7 H, multiplets), 2.97 (multiplet), 2.9 to 3.4 (multiplet). The latter multiplet appeared to be two triplets. The area from 2.9 to 3.4 was approximately 4 H. The n.m.r. spectrum was identical with the natural abundance *N*-butyl methanesulfonamide, except for the methyl peak at 2.97 p.p.m. Mass spectrum: a deuterium analysis was done using the peaks at *m/e* 79, 80, 81, and 82 (CH_3SO_2+). Relative intensities were 25.2, 100, 2.7, and 5.7, respectively. The composition was calculated to be:

Methyl Group	Mole %
CH_3	20.2
CH_2D	79.8
CHD_2	0
CD_3	0

L. Reaction of Methanesulfonyl Chloride with Tributylamine and Deuterium Oxide

A solution was prepared containing tributylamine (7.782 g, 42.0 mmole) and deuterium oxide (1.00 ml, 55.3 mmole) in dimethoxyethane (25 ml). It was added, with swirling, to a solution of methanesulfonyl chloride (253 mg, 2.21 mmole) in dimethoxyethane (25 ml).

The reaction was allowed to stand at room temperature

for 1 hr, after which the solvent was evaporated, ether added, and an extraction carried out with 5% sodium hydroxide. The aqueous layer was evaporated to dryness and benzene added. Phosphorus pentachloride was added, and the mixture warmed gently for 15 min.

The sulfonyl chloride was isolated by cautiously adding water and carrying out an extraction with ether. The product was distilled (cold finger apparatus) and obtained in low yield (60 mg). N.m.r. spectrum ($CDCl_3$): triplet at δ 3.63. A close examination revealed a singlet superimposed on the triplet. An integration by counting squares gave a ratio of areas of 1 : 9.3, respectively. This corresponds to a composition of 4 mole % CH_3 and 96 mole % CH_2D. There was no evidence of any CHD_2.

V. DETERMINATION OF EQUILIBRIUM CONSTANTS OF TERTIARY AMINES

A. Ionization Constants of Tertiary Amines in Water

A solution was prepared containing a suitable quantity of a tertiary amine in distilled water. A known volume of this solution was titrated against 0.200*M* standard hydrochloric acid at 22 ± 1°C, and the pH was recorded at

suitable intervals. A glass and calomel electrode was used with a Radiometer Model 25E pH meter, equipped with a scale expander. Buffer solutions were used to calibrate the instrument.

The following equation was used to calculate the apparent ionization constant K_B':

$$K_B' = \frac{[OH^-][BH^+]}{[B]}$$

Several points along the titration curve (before the equivalence point) were chosen and the pH and titer determined. Thus values for $[OH^-]$ and $[BH^+]$ were calculated, using $[Cl^-] = [BH^+]$ for the latter. The exact initial base concentration c was calculated from the equivalence point, and the concentration of free base [B] was $c-[BH^+]$. No corrections were made for ionic strength.

The value of K_B' obtained as described above was used to find pK_B', and pK_A' of the corresponding ammonium ion. When the pK_A' of the triethylammonium ion was obtained in this way, a value of 10.68 (lit. (31) 10.65) was obtained.

1,4-Diazabicyclo[2,2,2]octane (DABCO)

Base solution: 183 mg (0.016*M*) of DABCO in 100 ml of solution (distilled water). 50.00 ml of this solution was used in the determination.

HCl solution: 0.2000*M*.

Equivalence point: 3.979 ml.

pH	Titer (ml)	K'_B	pK'_B	pK'_A
8.65	2.00	4.51×10^{-6}	5.35	8.65
8.45	2.50	4.76×10^{-6}	5.32	8.68
8.20	3.00	4.83×10^{-6}	5.32	8.68
7.92	3.40	4.89×10^{-6}	5.31	8.69
7.58	3.70	5.03×10^{-6}	5.30	8.70

average $pK'_A = 8.68$

The values above refer to the first ionization constant. The titration curve showed no evidence of a second equivalence point.

N,N-*Diisopropylethylamine*

Base solution: approximately 208 mg (0.0161*M*) of diisopropylethylamine in 100 ml of solution (distilled water). Some of the difficultly soluble amine did not dissolve. The solution was filtered, and 49.2 ml of this solution was used in the determination.

HCl solution: 0.2000*M*.

Equivalence point: 3.169 ml.

pH	Titer (ml)	K'_B	pK'_B	pK'_A
11.11	1.50	1.76×10^{-3}	2.75	11.25
10.91	2.00	1.87×10^{-3}	2.73	11.27
10.63	2.50	2.00×10^{-3}	2.70	11.30
10.43	2.75	2.18×10^{-3}	2.66	11.34
9.96	3.00	1.92×10^{-3}	2.72	11.28

average $pK'_A = 11.29$

B. Equilibrium Constants of Tertiary Amines in Dimethoxyethane

The general procedure was similar to the method outlined by Bayles and Chetwyn (35). A stock solution of known concentration of the tertiary amine in dimethoxyethane was prepared, and the stock solution was further diluted to obtain the working solution. An indicator stock solution was prepared, containing the reference acid 2,4-dinitrophenol (184.8 mg in 100 ml, diluted 50 times, $2.008 \times 10^{-4} M$) in dimethoxyethane.

Exactly 5.0 ml of the indicator solution was placed in a 10 ml volumetric flask, and a known quantity of the base working solution was added. The solution was made up to the mark with dimethoxyethane and placed in a 1.0 cm quartz cell. The ultraviolet spectrum was obtained on the Cary 14 ultraviolet spectrophotometer at 25°C. The spectrum of the 2,4-dinitrophenoxide anion (ε_{400} = 10,900) was obtained by using an excess of base, and was identical to the spectrum reported in the literature (35). The absorption of the acid form was very low ($\varepsilon = \sim 100$) at 400 mμ.

Several different solutions were prepared for each determination, having identical indicator concentrations but different base concentrations. Excellent isosbestic points (at about 320 mμ) were obtained for each determination.

In every case the equilibrium constant was found to

obey the following expression:

$$K = \frac{[^{+}BH\cdots In^{-}]}{[B][HIn]}$$

The concentration of the complex was found by measuring the absorbance, A, of the solution in the u.v. at 400 mμ. The free base concentration [B] was found by subtracting $[^{+}BH\cdots In^{-}]$ from the total base concentration c. The free indicator concentration [HIn] was found by subtracting $[^{+}BH\cdots In^{-}]$ from the initial indicator concentration.

Quinuclidine

Base stock solution: 2.235 g of quinuclidine in 250 ml of dimethoxyethane ($8.04 \times 10^{-2} M$). Diluted 200 times to obtain the working solution.

Base sol'n

(ml)	c (M)	A (400 mμ)	K	Log K
.50	2.01×10^{-5}	.208	2.6×10^{5}	5.41
1.00	4.02×10^{-5}	.406	2.1×10^{5}	5.32
1.50	6.03×10^{-5}	.606	2.7×10^{5}	5.43
4.00	16.08×10^{-5}	1.004	2.2×10^{5}	5.34

average K = 2.4×10^{5}

average log K = 5.38

1,4-Diazabicyclo[2,2,2]octane (DABCO)

Base stock solution: 113.5 g of DABCO in 100 ml of dimethoxyethane ($1.013 \times 10^{-2} M$). Diluted 50 times to obtain working solution.

Base sol'n

(ml)	c (M)	A (400 mμ)	K	Log K
1.50	3.04×10^{-5}	.238	3.24×10^{4}	4.51
2.50	5.06×10^{-5}	.377	3.29×10^{4}	4.52
3.50	7.08×10^{-5}	.505	3.49×10^{4}	4.54
5.00	10.13×10^{-5}	.664	3.82×10^{4}	4.58

average K = 3.5×10^{4}

average log K = 4.54

Trimethylamine

Base stock solution: 2.5 ml of cold (-10°) trimethylamine in 200 ml of cold dimethoxyethane, then diluted 25 times. The concentration of the volatile amine was found by titration (see procedure in Kinetics section) to be 2.612 x $10^{-3}M$. The solution was checked from time to time by titration, and the concentration was found to be essentially constant. The stock solution was further diluted 5 times to obtain the working solution.

Base sol'n

(ml)	c (*M*)	A (400 mμ)	K	Log K
1.00	5.22×10^{-5}	.308	1.64×10^{4}	4.22
1.50	7.83×10^{-5}	.389	1.29×10^{4}	4.11
2.50	13.06×10^{-5}	.561	1.33×10^{4}	4.12
3.50	18.28×10^{-5}	.653	1.20×10^{4}	4.18

average K = 1.4×10^{4}

average log K = 4.13

N,N-*Dimethylethylamine*

Base stock solution: 1.436 g of dimethylethylamine in 250 ml of dimethoxyethane, then diluted 25 times (2.924 x $10^{-3}M$; found by titration - see previous experiment). The stock solution was further diluted 5 times to obtain the working solution.

Base sol'n

(ml)	c (M)	A (400 mμ)	K	log K
1.00	5.85×10^{-5}	.282	1.07×10^{4}	4.03
1.50	8.77×10^{-5}	.380	1.01×10^{4}	4.01
2.50	14.62×10^{-5}	.537	$.995 \times 10^{4}$	4.00
5.00	29.24×10^{-5}	.742	$.940 \times 10^{4}$	3.97

average K = 1.0×10^{4}

average log K = 4.00

Triethylamine

Base stock solution: 100.8 mg of triethylamine in 100 ml of dimethoxyethane ($9.96 \times 10^{-3} M$). Diluted 25 times to obtain the working solution.

Base sol'n (ml)	c (M)	ABS (400 mμ)	K	log K
1.00	3.98×10^{-5}	.224	1.33×10^{4}	4.12
1.50	5.98×10^{-5}	.301	1.18×10^{4}	4.07
2.50	9.96×10^{-5}	.460	1.26×10^{4}	4.10
5.00	19.93×10^{-5}	.689	1.25×10^{4}	4.09

average K = 1.3×10^{4}

average log K = 4.10

N,N-*Diisopropylethylamine*

Base stock solution: 136 mg of diisopropylethylamine in 100 ml of dimethoxyethane ($1.052 \times 10^{-2} M$). Diluted 5 times to obtain the working solution.

Base sol'n

(ml)	c (M)	A (400 mμ)	K	log K
.50	1.052×10^{-4}	.215	2.86×10^{3}	3.46
1.00	2.104×10^{-4}	.370	2.89×10^{3}	3.46
1.50	3.156×10^{-4}	.490	3.03×10^{3}	3.48
2.50	5.260×10^{-4}	.643	3.04×10^{3}	3.48
5.00	10.52×10^{-4}	.860	3.75×10^{3}	3.57

average K = 3.1×10^{3}

average log K = 3.49

Tributylamine

Base stock solution: 3.711 g of tributylamine in 250 ml of dimethoxyethane ($8.01 \times 10^{-2} M$). Diluted 25 times to obtain the working solution.

Base sol'n

(ml)	c (M)	A (400 mμ)	K	log K
1.00	3.20×10^{-4}	.349	1.69×10^{3}	3.23
5.00	16.02×10^{-4}	.743	1.47×10^{3}	3.17

average K = 1.6×10^{3}

average log K = 3.20

N-*Methylmorpholine*

Base stock solution: 2.028 g of *N*-methylmorpholine in 250 ml of dimethoxyethane ($8.01 \times 10^{-2} M$). Diluted 5 times to obtain the working solution.

Base sol'n

(ml)	c (*M*)	A (400 mμ)	K	log K
1.00	1.60×10^{-3}	.244	1.82×10^{2}	-2.26
1.60	2.56×10^{-3}	.351	1.87×10^{2}	-2.27
2.50	4.00×10^{-3}	.441	1.70×10^{2}	-2.23
5.00	8.01×10^{-3}	.622	1.65×10^{2}	-2.22
5.00[a]	40.05×10^{-3}	.889	1.08×10^{2}	-2.03

average K = 1.7×10^{2}

average log K = 2.23

a. Stock solution.

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EXPERIMENTAL

Infra-red spectra were recorded on a Beckman IR-10 spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer using 1.0 cm quartz cells. Nuclear magnetic resonance (n.m.r.) spectra were obtained on Varian A-60, T-60, and HA-100 instruments; signals are expressed in parts per million (p.p.m.) downfield from tetramethylsilane as internal standard (δ scale). Mass spectra were obtained on a Varian M-66 instrument. Refractive indices were determined with a thermostatically controlled Bausch and Lomb refractometer. Melting points were determined on a Kofler hot stage, and are uncorrected.

Methylene chloride and 1,2-dimethoxyethane were distilled from calcium chloride and calcium hydride, respectively. Methanesulfonyl chloride was distilled before use, and phenylmethanesulfonyl chloride was recrystallized from carbon tetrachloride. Triethylamine and pyridine were distilled after refluxing over calcium hydride, and tributylamine was distilled from potassium hydroxide pellets. Quinuclidine and 1,4-diazabicyclo[2,2,2]octane were sublimed. Deuterium oxide (99.8% D_2O) was supplied by Stohler Isotope Chemicals,